THIS PAGE BLANK (USPTO)

-1-

PROCESS FOR HYDROXYALKYLATING
CARBOXYLIC ACID-FUNCTIONALIZED MATERIALS

BACKGROUND OF THE INVENTION

5   Field of the Invention

        The present invention relates broadly to a process
for hydroxyalkylating carboxylic acid-functionalized
materials. More specifically, this invention provides a
process for preparing primary hydroxyl-terminated polymers
10   from carboxylic acid-terminated polymers, such as carboxylic
acid-terminated butadiene nitrile co-polymers ("CTBNs"),
using a carbocyclic carbonate, such as ethylene carbonate,
or a carbocyclic sulfite, such as ethylene sulfite.

Brief Description of the Prior Art

15   Hydroxyl-terminated butadiene nitrile co-polymers
("HTBNs") are known, and are generally useful as extenders
with difunctional polymerizable materials to add toughness
to adhesive compounds, caulking compounds and potting
compounds. HTBNs react rapidly through their terminal
20   hydroxyl groups with, for instance, organic diisocyanates to
form solid, high molecular weight materials of low
fusibility. [See e.g., U.S. Patent No. 3,551,472 (Siebert).]
They are also used in particular to form block prepolymer

SUBSTITUTE SHEET (RULE 26)

resins, as taught by U.S. Patent No. 4,295,909 (Baccei), the disclosure of which is hereby incorporated herein by reference.

Certain HTBNs, such as one available under the
5 tradename "HYCAR" 1300X29, have been manufactured commercially for some time by the B.F. Goodrich Co., Akron, Ohio. To that end, B.F. Goodrich's U.S. Patent No. 4,444,692 (Okamoto) claims a process for making such HTBNs from carboxylic acid-terminated butadiene nitriles ("CTBNs")
10 using ethylene oxide. In fact, this process is believed to have been used to manufacture commercial quantities of HTBNs. Ethylene oxide, however, is a gaseous and hazardous material which is highly toxic and thus, at least for this reason, is undesirable as a reactant. Accordingly,
15 different processes, particularly ones which did not employ the gaseous and highly toxic ethylene oxide and which achieve the desired result, would be viewed as desirable.

Another method of preparing HTBNs from CTBNs involves the use of diols. Indeed, B.F. Goodrich's '472
20 patent discloses such a method, employing diols having three to six carbon atoms in an acid-catalyzed direct esterification to yield primary hydroxyl-terminated materials with a straight-chain three to six carbon atom unit between the carboxylic acid linkage and the hydroxyl
25 terminus. However, this process has certain undesirable features, namely the use of a large excess of the diol which is particularly troublesome to remove upon completion of the reaction, and trans-esterification which results in an increase of the molecular weight of the so-formed HTBN which
30 in turn increases the viscosity and reduces the hydroxyl number of the resultant HTBN.

Hydroxyamide-terminated equivalents to HTBN have also been prepared by amidation of CTBN with aminoalcohols. See B.F. Goodrich's U.S. Patent No. 4,489,008 (Riew).
35 However, such process is not particularly suitable for large-scale commercial production as aminoalcohols are not only toxic, but are used in molar excess to CTBN. Since residual aminoalcohols are difficult to remove, the final

SUBSTITUTE SHEET (RULE 26)

polymer is frequently treated with maleate esters and the
like to ensure complete aminoalcohol removal. This results
in the formation of low molecular weight reactive
plasticizers, which adversely affect the toughness of
urethane resins produced from the so-prepared
hydroxyamide-terminated material.

        Methods of introducing an alkyl hydroxyl
functional group in place of an acidic hydrogen, such as
from a carboxylic acid or a phenol, are known, an example of
which involves the use of ethylene carbonate together with
basic materials such as potassium carbonate and the like.
See U.S. Patent No. 5,019,629 (Woods). However, use of
potassium carbonate in the realm of the conversion desired
herein fails to yield desired HTBN. Also, U.S. Patent No.
2,448,767 (Carlson) speaks to the hydroxyethylation of
certain compounds including carboxylic acids generally using
ethylene carbonate or ethylene sulfite, either in the
absence of a catalyst or in the presence of an acidic one
like sulfuric acid or organic esters thereof, or an alkali
carbonate. However, use of either no catalyst or an acidic
one in the realm of the conversion desired herein also fails
to yield desired HTBN.

        Other methods for hydroxyalkylating materials,
such as polysaccharides, are known. For instance, U.S.
Patent No. 4,474,951 (Pope) speaks to and claims the
hydroxyalkylation of polysaccharides using an alkylene
carbonate in the presence of a catatytic amount of a
quartnery ammonium halide.

        In addition, U.S. Patent No. 4,513,146 (Thompson)
speaks to the use of carbonates to form esters of carboxylic
acids. The '146 patent is silent, however, as to cyclic
carbonates for such use.

        U.S. Patent No. 4,310,707 (Strege), however,
speaks to and claims a method of hydroxyalkyating phenols
and thiophenols using cyclic organic carbonate compounds and
sodium stannate as the catalyst. U.S. Patent No. 4,261,922
(Kem) also relates to hydroxyl alkylation reactions to
prepare ether compounds from cyclic organic carbonate

compounds and phenols contacted in the presence of potassium
iodide catalyst. And U.S. Patent No. 4,266,046 (Wu) speaks
to and claims a process for preparing esters of
polycarboxylic acids which includes reacting cyclic
carbonates with a polycarboxylic acid in the presence of an
alkylammonium halide. The polycarbocyclic acids are
exemplified as hydrocarbon radicals having from two to four
carboxylic acid groups, and are selected from substituted
aromatic acids, cyclohexyl acids and short chain acids.

In the context of low molar mass compounds, <u>see</u>
Yoshino, <u>J. Chem. Soc., Perkins Trans. I</u>, (11) 1266 (1977).

Nevertheless, it would be desirable to demonstrate
yet another way in which an hydroxyl group could be
introduced to a carboxylic acid group, particularly in the
case of the preparation of HTBNs (such as HTBNs having a
lower alkyl, <u>e.g.</u>, a two or three carbon unit, between the
carboxylic acid functionality and the hydroxyl group), which
does not involve the use of the hazardous reagent, ethylene
oxide, to achieve the desired result.

SUMMARY OF INVENTION

The present invention is directed to a process for
hydroxyalkylating carboxylic acid group-functionalized
material. More specifically, this invention provides a
process for preparing an hydroxyl-functionalized material,
which includes the step of reacting a carboxylic
acid-functionalized material with an amount of a carbocyclic
carbonate or carbocyclic sulfite in the presence of a phase
transfer catalyst under conditions sufficient to form the
hydroxyl-functionalized material. In a particularly
desirable aspect of the invention, the funtionalized
material should be a nitrile rubber, such as those found in
a liquid or melt phase. The amount of carbocyclic carbonate
or carbocyclic sulfite should of course be sufficient to
convert the carboxylic acid groups of the carboxylic
acid-functionalized material into an hydroxyl-functionalized
material.

By the process of the present invention, therefore, a carboxylic acid-functionalized material is converted into an hydroxyl-functionalized material having a lower alkyl linkage (such as a two or three carbon alkyl

5   linkage) between the prior carboxylic acid group (now an ester linkage) and the newly-formed hydroxyl group.

Also, more generally, the present invention provides a method of using carbocyclic carbonates or carbocyclic sulfites, such as ethylene carbonate or

10   propylene carbonate (such as 1,3-propylene carbonate), or ethylene sulfite or propylene sulfite (such as 1,3-propylene sulfite), respectively, in the presence of a phase transfer catalyst as a replacement reactant in synthetic schemes presently calling for the use of carbocyclic oxides, such as

15   ethylene oxide or propylene oxide, respectively. In such use, the carbocyclic carbonates or carbocyclic sulfites are capable of introducing an alkyl hydroxyl group to a reactive group having an acidic hydrogen, such as a carboxylic acid group.

20   The present invention also provides a method of purifying the so-formed hydroxylated material which includes the step of contacting the reaction mixture with an appropriate amount of an amphoteric treating agent. This purifying treatment method avoids the conventional use of a

25   solvent to accomplish that objective.

The process of the present invention treats a carboxylic acid-functionalized material, such as CTBN, with an hydroxyalkylating reagent, such as a carbocyclic carbonate or carbocyclic sulfite, in the presence of a phase

30   transfer catalyst to provide a corresponding hydroxyl-functionalized material, such as HTBN, in a manner which is simple, safe and commercially viable. As an unexpected result, in the case of HTBN, the so-formed HTBN demonstrates certain properties unlike those of

35   conventionally prepared HTBNs, which may be attributable to the lack of ethylene glycol in the HTBN, see infra. The lack, or substantial lack, of such impurity results in improved performance for certain applications compared to

SUBSTITUTE SHEET (RULE 26)

HTBN derived from conventional processes (e.g., using ethylene oxide). For instance, urethane block co-polymers may be prepared therefrom with improved toughness.

In the process according to the present invention, the hydroxyalkylating reagent, as well as the phase transfer catalyst, are non-toxic and require neither special handling conditions nor equipment. The process according to this invention also does not require a solvent for reaction and in one aspect does not require a solvent for separation or purification. In addition, at least the prior process which employs ethylene oxide also requires a trialkyl amine catalyst, the entire removal of which at the completion of the reaction is difficult and the presence of which (even in residual amounts) frequently results in premature polymerization of block resins formed from HTBN.

The present invention will be more readily appreciated by those of skill in the art after a reading of the detailed description of the invention which follows, together with the illustrative examples presented thereafter.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, this invention relates to a process for reacting carboxylic acid-functionalized polymeric materials, such as terminal and/or pendant carboxylic acid-functionalized materials, with an amount of carbocyclic carbonate or carbocyclic sulfite, such as ethylene carbonate or ethylene sulfite, respectively, sufficient to cause formation of hydroxyl-functionalized materials by conversion of carboxylic acid groups to hydroxyl groups with a lower alkyl linkage between the ester linkage and the newly-formed hydroxyl group.

The hydroxyalkylating reagent appropriate to convert terminal carboxylic acid groups to corresponding terminal hydroxyl groups may be chosen from a variety of materials. Of particular interest are carbocyclic carbonates and carbocyclic sulfites. For instance, where a primary hydroxyl is desirable as a terminal group, an

unsubstituted carboxylic material may be chosen. That is, in the event a two or a linear three carbon linkage is desired between the ester linkage and the terminal hydroxyl group, and carbocyclic carbonate is desired as the

5   hydroxyalkylating reagent, ethylene carbonate or 1,3-propylene carbonate should be used. Where a mixture of primary and secondary hydroxyl groups is desired as the terminal groups and carbocyclic carbonates are desired as hydroxyalkylating reagent, 2-methyl-1,2-ethylene carbonate

10   or 3-methyl-1,3-propylene carbonate should be used. If secondary hydroxyl groups alone are desired, then 1,2-dimethyl-1,2-ethylene carbonate or 1,3-dimethyl-1,3-propylene carbonate should be used. Similarly, 1,1-dimethyl-1,2-ethylene carbonate or

15   1,1-dimethyl-1,3-propylene carbonate should yield a mixture of primary and tertiary hydroxyl end groups; 1,1,2-trimethyl-1,2-ethylene carbonate or 1,1,2-trimethyl-1,3-propylene carbonate should yield a mixture of secondary and tertiary hydroxyl end groups; and

20   1,1,2,2-tetramethyl-1,2-ethylene glycol or 1,1,2,2-tetramethyl-1,3-propylene glycol should yield tertiary hydroxyl end groups.

        As for carbocyclic sulfites, ethylene sulfite and propylene sulfites (such as 1,2-propylene sulfite and

25   1,3-propylene sulfite) should be used. Of course, combinations of carbocyclic carbonates and carbocyclic sulfites may also be used.

        Generally, a stoichiometric or a slight excess amount of the carbocyclic carbonate or carbocyclic sulfite

30   may be used for each equivalent of carboxylic acid group present on the carboxylic acid-functionalized material. Desirably, in the case of a carbocyclic carbonate, a slight excess may be used, such as about 2.2 equivalents for each equivalent of carboxylic acid-functionalized material having

35   two carboxylic acid groups.

        As noted above, the reaction desirably proceeds in the presence of a phase transfer catalyst. The catalyst may be any material capable of accelerating the rate of

SUBSTITUTE SHEET (RULE 26)

hydroxyalkylation and minimizing undesirable side reactions. Ordinarily, the catalyst is a quaternary ammonium halide and may be used in an amount in the range of about 0.005 to about 0.5 equivalents, with about 0.01 to about 0.1

5 equivalents being preferred, for each equivalent of the carboxylic acid-functionalized material. Phosphonium halides (such as triphenyl phosphonium halides like triphenyl phosphonium bromide) and sulfoniun halides may also be used. See e.g., the '046 patent, the disclosure of

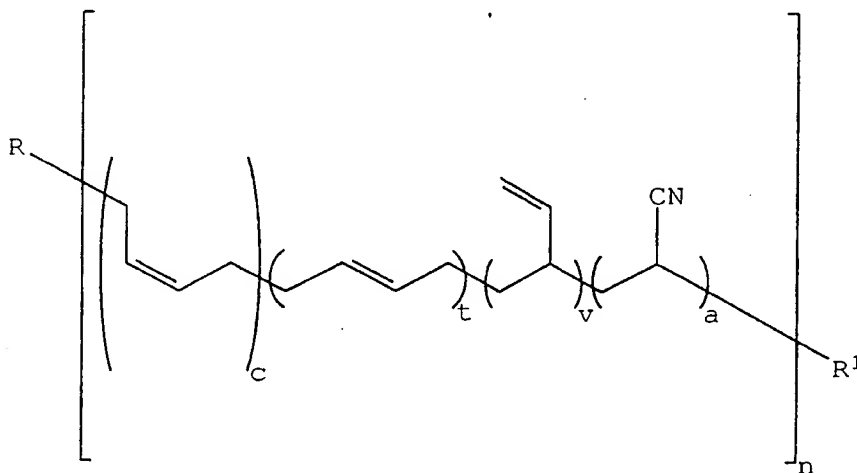10 which is hereby expressly incorporated herein by reference.

Specific examples of suitable quaternary ammonium halides include alkaryl ammonium halides, such as benzyltrimethyl ammonium chloride and tetralkyl ammonium halides, such as tetraethyl ammonium halides or tetrabutyl

15 ammonium halides like bromides or iodides. Other desirable materials useful as the phase transfer catalyst include crown ethers and calixarenes. Of course, combinations of these materials may also be used. A particularly desirable catalyst in connection with the process of the present

20 invention is tetraethylammonium iodide.

The carboxylic acid-functionalized materials used in the process of the present invention may be selected from a wide variety of carboxylic acid-functionalized polymers having mono- or poly-carboxylic acid groups. Included among

25 such materials are alkenoic carboxylic acid-functionalized materials, polymers of dienes, such as butadiene, co-polymers of dienes and vinylnitriles, such as butadiene-acrylonitrile, and alkyl acrylates, which may be prepared, for example, by known processes, such as described

30 in B.F. Goodrich's U.S. Patent No. 3,285,949 (Siebert), and the like.

Other suitable materials include carboxylic acid-functionalized versions of liquid and solid polymers of conjugated diene monomers or mixtures of these monomers with

35 co-polymerizable monomers. Examples include olefins (e.g., isobutylene), aryl olefins and substituted aryl olefins (e.g., styrene, p-chlorostyrene, p-methoxystyrene, alpha methyl styrene, vinyl naphthalene, and the like);

SUBSTITUTE SHEET (RULE 26)

unsaturated organic acids (<u>e.g.</u>, acrylic and methacrylic
acids); alkyl esters of acrylic and methacrylic acids (<u>e.g.</u>,
methyl acrylate, methyl methacrylate, butylacrylate, and the
like); nitriles of acrylic and methacrylic acids (<u>e.g.</u>,
acrylonitrile, methacrylonitrile, and the like); vinylidene
chloride; vinyl ketones (<u>e.g.</u>, methyl vinyl ketones); vinyl
ethers; vinyl carbazole; vinyl furan; vinyl pyridine; and
the like. These liquid or solid polymers may be prepared by
conventional methods including mass, emulsion and solution
polymerization methods. <u>See</u> U.S. Patent No. 3,346,631
(Boyer), the disclosure of which is hereby expressly
incorporated herein by reference.

     A general representation of certain desirable
carboxylic acid-functionalized polymers suitable for use
with the subject invention include those within structure:

where R and R^1 may be the same or different and may be
selected from COOH or CAA^1-X-COOH, where A and A^1 may be the
same or different and may be selected from hydrogen,
halogen, cyano, or linear or branched alkyl groups having
from 1 to about 5 carbon atoms and X may be selected from
linear or branched alkyl groups having from 2 to about 5
carbon atoms, such as methylene, ethylene, propylene and the
like.

     The fraction of repeat units of the contributing
repeat fragment are represented, by c+t+v+a=1, and n
represents the average degree of polymerization.

Examples of carboxylic-acid functionalization
through the CAA'-X-COOH group include

5

10   Specific examples of carboxylic
acid-functionalized polymers which may benefit from the
process of the present invention include acrylic and
methacrylic acid polymers and co-polymers, carboxylic
acid-functionalized hydrogenated butadiene nitrile
15   co-polymers, carboxylic acid-terminated poly(isobutylene),
carboxylic acid-terminated polyesters, polyamides,
polyurethanes and polymeric acids derived from maleic
anhydride co-polymers, and carboxylic acid-terminated
polyethylene, polybutadiene, polyisoprene,
20   poly(butadiene-co-acrylonitrile), poly(isobutylene),
poly(butadiene-co-styrene),
poly(butadiene-co-acrylonitrile-co-acrylic acid), poly(ethyl
acrylate), poly(ethyl acrylate-co-n-butyl acrylate),
poly(n-butyl acrylate-co-acrylonitrile), poly(butyl
25   acrylate-co-styrene), and the like. Of course, carboxylic
acid-functionalized block and graft co-polymers may also be
hydroxyalklated according to the present invention.
     Of particular interest is CTBN, available
commercially from B.F. Goodrich under the "HYCAR" trademark,
30   such as "HYCAR" 1300X31. CTBN generally has a number
average molecular weight in the range of about 3,100 to
about 4,200, with about 3,800 being desirable, an AN content
in the range of 0 to about 26% by weight, with about 10%
being desirable [polymer without AN in the case of CTBN, is
35   carboxy-terminated polybutadiene (CTB)], and terminal groups
R and R^1 as shown above. With respect to contributing
repeat unit fragments, CTBN has c+t+v=1-a, where generally

a=0.1, and n is in the range of about 5 to about 750, with about 53 to about 74 being desirable.

Typically, the process of the present invention may be performed by contacting together the carboxylic acid-functionalized polymer, such as CTBN, a carbocyclic carbonate, such as ethylene carbonate, and a phase transfer catalyst, such as tetrabutyl ammonium iodide, for a period of time in the range of about 0.5 hours to about 2 hours, with about 1 hour being desirable, at a temperature in the range of about 125 to about 150°C. Of course, variations of these time and temperature parameters may be desirable depending on the identity and quantity of the starting materials used. Such variations are routine and within the ambit of knowledge of those persons of skill in the art.
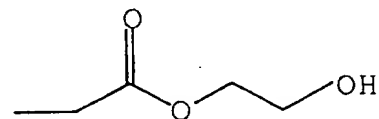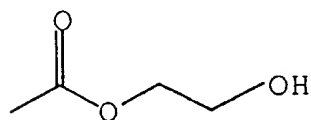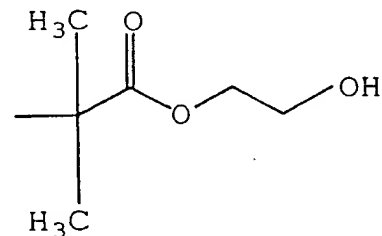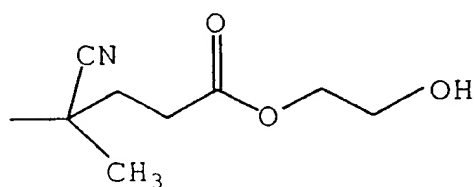
The so-formed hydroxyl-functionalized polymer, such as HTBN, may thereafter be used, if desired, as generated directly from the reaction mixture, or coagulated with liquid media, such as methanol and/or water, physically separated, such as by decantation, and dried under vacuum. Alternatively, the so-formed hydroxyl-functionalized material may be treated with an amphoteric treating agent, as discussed _infra_, followed by physical separation, such as filtration.

It may be desirable to alter the reaction conditions in order to suit the particular reagents chosen. For example, while a liquid medium, such as a solvent, ordinarily is not required to perform the process of this invention, one may be desirable if, for instance, the carboxylic acid-functionalized polymer chosen is solid at the reaction temperature or if the hydroxyalkylating reagent is insoluble in the carboxylic acid-functionalized polymer at that temperature. Appropriate solvents or liquid media capable of dissolving or dispersing the carboxylic acid-functionalized polymer and the hydroxyl-functionalized polymer formed therefrom include acetone, methyl ethyl ketone, cyclohexanone, tetrahydrofuran, dioxane, toluene, xylene(s) and combinations thereof. Ordinarily, however, the hydroxyalkylating reagent, such as carbocyclic

-12-

carbonate, may be used in an excess amount to ensure
fluidity and accomplish satisfactory heat transfer. Those
persons of skill in the art should of course make
appropriate choices for the liquid media, when used, to

5   achieve the desired results.

The hydroxyl-functionalized polymers produced by
the process of the present invention include, of course,
hydroxyalkylated versions of any of the wide variety of
carboxylic acid-functionalized polymers indicated above.

10   For instance, hydroxyalkylated versions of the carboxylic
acid-functionalized polymer include those where R and R^1 may
be selected from $COO-X^1-OH$ or $CAA^1-X-COO-X^1-OH$, where A, A^1
and X are as defined above and X^1 is as defined by X.

Examples of hydroxyalkylated versions of

15   carboxylic acid-functionalized polymers through the
$COO-X^1-OH$ or the $CAA^1-X-COO-X^1-OH$ group therefore include

20

25

30   Specific examples of hydroxyl-functionalized
polymers which may be prepared in accordance with the
process of the present invention include hydroxyl-terminated
polyethylene, polybutadiene, polyisoprene,

35   poly(butadiene-co-acrylonitrile),
poly(butadiene-co-styrene),
poly(butadiene-co-acrylonitrile-co-acrylic acid), poly(ethyl
acrylate), poly(ethyl acrylate-co-n-butyl acrylate),

SUBSTITUTE SHEET (RULE 26)

poly(n-butyl acrylate-co-acrylonitrile), poly(butyl
acrylate-co-styrene), and the like.

Specific examples of hydroxyl-functionalized
copolymers of butadiene containing in excess of about 50% by
5   weight of butadiene with the remainder being at least one
co-polymerizable olefinically unsaturated monomer, such as
acrylonitrile, alkyl acrylates and methacrylates, acrylic
and methacrylic acid, and other materials known to
free-radically co-polymerize with butadiene, such as
10 styrene(s) and derivatives thereof, and other related
polymerizable materials, such as are disclosed, for
instance, in the '909 patent.

After the hydroxyl-functionalized polymers are
formed, they are separated from the reaction mixture by
15 precipitation in a suitable non-solvent, such as methanol.
This provides purified polymer free of a phase transfer
catalyst, ethylene carbonate and ethylene glycol (if
ethylene carbonate is used as the carbocylic carbonate),
after removal of solvent. The so-formed polymer may also be
20 purified through contact with an amphoteric treating agent,
which removes all or substantially all of the catalyst.
Such amphoteric treating agents and general uses therefor
are discussed in detail in U.S. Patent Nos. 5,371,181
(Glaser) and 5,399,624 (Glaser).

25   The amphoteric treating agents so noted may be
chosen from silicated magnesium oxide, magnesium oxide,
magnesium hydroxide, calcium hydroxide, barium oxide and
barium hydroxide. Of course, combinations thereof may also
be employed, if desired. The average particle size of the
30 amphoteric treating agent should be in the range of about 2
to about 200 microns. A particularly desirable amphoteric
treating agent is "MAGNESOL" Polysorb 30/40 hydrated
silicated magnesium oxide (commercially available from The
Dallas Group of America Inc., Liberty Corner, New Jersey),
35 which has a particle size in the range of from about 2 to
about 200 microns, and an average particle size of about 50
microns.

The use of such amphoteric treating agents allows
for adsorption of the catalyst from the reaction mixture and
avoids the introduction of a solvent, such as methanol,
which must thereafter be removed, and which is flammable.

5   After treatment, the amphoteric treating agents may be
removed by physical means, such as filtration. The
desirability of using the amphoteric treating agents is
therefore seen not only as a purification measure, but also
as a safety measure, as well as a cost-saving measure.

10   Accordingly, it is seen that a number of
significant advantages may be realized by the process of the
present invention, particularly when compared with known
processes. For instance, a relatively innocuous coreactant
is employed in the process hereof (i.e., a carbocyclic

15   carbonate, such as ethylene carbonate, or a carbocyclic
sulfite, such as ethylene sulfite) as compared with the
coreactant used in certain known processes (i.e., ethylene
oxide). Another significant advantage is that fewer
impurities are formed through the use of a carbocyclic

20   carbonate or carbocyclic sulfite reagent, and impurities
originating from ethylene oxide or the amine catalyst used
therewith are no longer present.

What's more, while removal of the amine catalyst
in prior processes was also seen as important for promoting

25   shelf-stability of hydroxyl-terminated polymers (see e.g.,
the '692 patent) and stabilizing formulations containing
hydroxyl-terminated polymers and acrylate diluents (such as
through the observation of less gelling of the diluent
component) used for making block resins (see e.g., the '909

30   patent), use of an acidic material to accomplish that
objective was viewed as disadvantageous, particularly when
the so-formed hydroxyl-terminated polymer was destined for
use in urethane formation (such as in the preparation of
block resins), as the presence of an acidic material may

35   retard urethane formation.

HTBNs so formed in accordance with the process of
the present invention, as well as HTBNs generally, have many
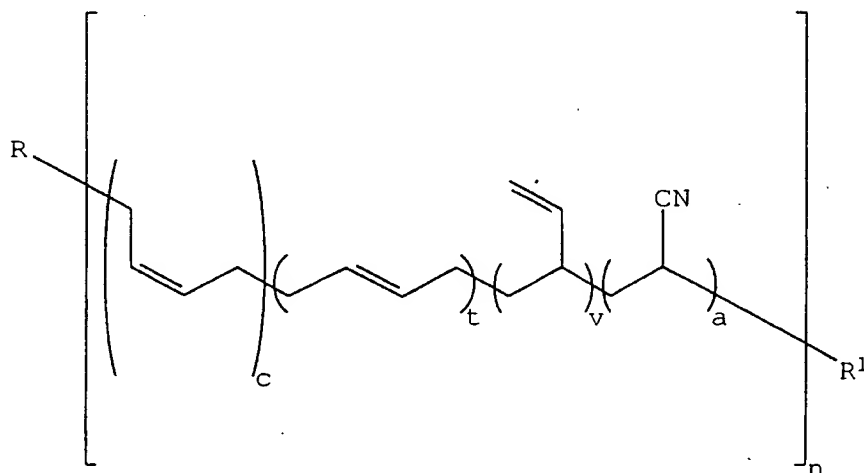uses, though a particularly desirable one is as intermediate

monomers in the formation of block prepolymer resins. Block
prepolymer resins may be viewed as one-component,
polymerizable block co-polymers having rigid and flexible
segments, with block resins having flexible segments derived

5   from HTBN being particularly useful in the preparation of
structural anaerobic adhesives. Products derived from such
resins are ordinarily characterized by a combination of high
adhesive strength, good cure through depth (surface
activation) and outstanding cohesive toughness. See the

10   '909 patent.

     Thus, an additional aspect of this invention
provides an adhesive and sealant composition having improved
thermal and impact properties and curable though gaps of
more than 40 mils.

15   Such a composition includes a reaction product of
the hydroxyl-functionalized material formed from reacting a
carboxylic acid-functionalized material with an
hydroxyalkylating reagent in the presence of a phase
transfer catalyst under conditions sufficient to form the

20   hydroxyl-functionalized material; a molar excess of
polyisocyanate and polyol, with the so-formed reaction
product subsequently being reacted with a molar excess of a
hydroxyalkyl or amino acrylate, or methacrylate; and an
initiator.

25   Of course, the carboxylic acid-functionalized
material may be one within the structure below:

BNSDOCID: <WO___9831655A1_I_>

where R and R¹ may be the same or different and may be
selected from COOH or CAA¹-X-COOH, with A and A¹ being the
same or different and being selected from hydrogen, halogen,
cyano or linear or branched alkyl groups having from 1 to
about 5 carbon atoms and X being selected from linear or
branched alkyl groups having from 2 to about 5 carbon atoms,
c+t+v+a=1, and n is an integer in the range of from about 5
to about 750.

The hydroxylating reagent may be selected from
carbocyclic carbonates and carbocyclic sulfites. The
polyisocyanate and the polyol may be ones which are aromatic
or cycloaliphatic. The initiator may be a free-radical
initiator or a photoinitiator.

A desirable adhesive and sealant composition along
these lines includes one where the polyisocyante is toluene
diisocyanate or 4,4'-diisocyanate diphenyl methane and the
reaction product is one from the reaction of
isocyantate-terminated hydrogenated bisphenol-A with toluene
diisocyanate.

Accordingly, HTBNs formed in accordance with the
present invention may be used to form block prepolymer
resins in accordance with the teaching of the '909 patent,
such as by chemically-linking two "pre-polymers" which are
subsequently "capped" with acrylate or methacrylate
functionality. In this way, a "flexible" polymeric
butadiene polyol segment of relatively low molecular weight
is reacted with a molar excess of a "rigid" diisocyanate,
such as toluene diisocyanate or methylene diisocyanate,
thereby forming urethane linkages. Thus, the resin
structures include a central flexible low glass transition
linear polymer which is chemically linked to relatively
short rigid segments, located at either end of the linear
polymer through urethane groups and capped with acrylate or
methacrylate groups.

The term "rigid" segment as used herein with
respect to block resins includes a segment or segments
containing aromatic, heterocyclic or cycloaliphatic rings,
with multiple segments joined by either fusing the rings or

by a minimum number of carbon atoms (<u>e.g.</u>, 1 to 2, if
linear, or 1 to about 6, if branched) such that there is
little or no flexing of the segments. The term "flexible"
segment as used herein with respect to block resins includes
a segment of primarily linear aliphatic moieties containing
internal unsaturation, with pendant functional groups, such
as aromatic, heterocyclic, cycloaliphatic, and the like, as
well as branching, also incorporated therein, provided no
substantial interference exists with the flexible nature of
the linear portion.

    The flexible polybutadiene or copolybutadiene
having functional groups containing an active hydrogen may
be reacted with a molar excess (<u>e.g.</u>, about 0.05 to about 6)
of polyisocyanate as to the concentration of the active
hydrogen-containing groups on the polybutadiene. In this
way, a product is assured which has an isocyanate group at
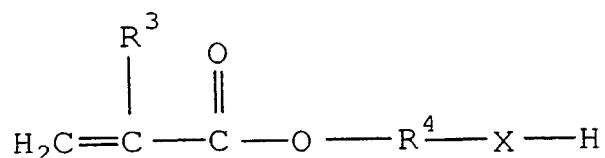each end of the polybutadiene segment.

    The rigid segment may be derived from the reaction
of cycloaliphatic diols, such as hydrogenated bis-phenol A,
with two equivalents of a diisocyanate, such as toluene
diisocyanate. The urethane resins are synthesized in the
presence of diluent monomers, such as triethylene glycol
dimethacrylate, which also have a significant influence on
the cured material properties. Such block resins derived
from HTBN have improved thermal, chemical and impact
resistance compared to other materials.

    By selection of appropriate flexible and rigid
segments, the material properties of the cured resins may be
optimized for adhesive applications. And in order to ensure
rapid and complete incorporation of the flexible segment
into the urethane polymer, it is desirable for the terminal
hydroxyl groups of the HTBN to be primary, rather than
secondary or tertiary.

    Block resins may be prepared at temperatures
within the range of from about room temperature to about
150°C, with temperatures within the range of from about 40°C
to about 120°C being particularly desirable. After addition
of the flexible diol to the isocyanate-functionalized rigid
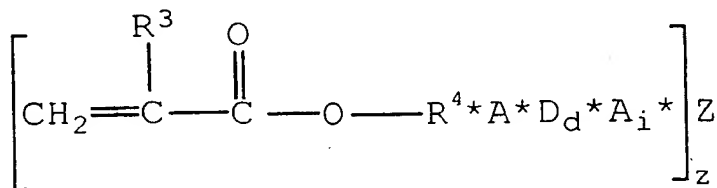
SUBSTITUTE SHEET (RULE 26)

segment, the reaction should be allowed to continue to proceed for a period of time of about 0.1 to about 24 hours. In addition, if desired, the reaction may be catalyzed, and unreactive diluents may also be used to control viscosity, bearing in mind of course that the presence of unreactive diluents may affect material properties of the cured resins.

The product of this reaction may be reacted with at least a molar equivalence, based on isocyanate group content, of an hydroxy or aminoalkyl acrylate or methacrylate to form an adhesive/sealant monomer (or prepolymer) capped at both ends with acrylate or methacrylate functionality, respectively. Esters suitable for such use are of a wide variety, although particularly desirable ones may be represented by:

$$H_2C=C \overset{\overset{\displaystyle R^3}{|}}{\underset{}{}} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R^4 - X - H$$

where X is O, S or NH, R^3 may be hydrogen, halides (e.g., chlorine) and alkyl groups (e.g., methyl and ethyl); and R^4 may be lower alkyl groups, such as linear, branched, or cyclic groups having 1 to about 8 carbon atoms, phenylene and naphthalene.

The fully-prepared monomeric block prepolymers may be represented by:

$$\left[CH_2=C \overset{\overset{\displaystyle R^3}{|}}{\underset{}{}} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R^4 * A * D_d * A_i * \right]_z Z$$

where R^3 and R^4 are as defined above; A is a polyisocyanate linkage; D is an aromatic, heterocyclic or cycloaliphatic polyol or polyamine group (e.g., a diol of a cycloaliphatic compound); Z is a polymeric or copolymeric polyol or poly radical of butadiene, the latter having a degree of

polymerization of from about 5 to about 150 and at least about 70 percent of the polybutadiene portion of the 1,4-configuration; z is an integer corresponding to the valency of Z; d is either 0 or 1; and i is 0 when d is 0, and otherwise is one less than the number of reactive hydrogen atoms of D. An asterisk indicates a urethane (-NH-COO-) or ureide (-NH-CO-NH-) linkage.

As noted above, the block prepolymer resins cure to a hard, tough resin, using any of a wide variety of known free radical initiators, which may be activated by redox, thermal or photo-initiated mechanisms.

Examples of such free radical initiators include (a) ones which perform through a redox mechanism such as benzoyl peroxide/N,N-dimethyl-p-toluidine, cumene hydroperoxide/o-benzoyl sulfimide/N,N-dimethyl-p-toluidine, and tributyl borane; (b) ones which perform under elevated temperature conditions such as benzoyl peroxide, and 2,2'-azobisisobutylnirtile; and (c) ones which perform through photo-initiators 2,2-dimethoxy-2-phenylacetophenone and benzoyl cyclohexanol.

In addition, while one aspect of the present invention as exemplified in the illustrative examples is directed to a novel process for the preparation of HTBN, as noted above, it may also be used to convert a wide range of carboxylic acid functionalized polymers and oligomers to the corresponding hydroxylated derivatives.

The following examples are provided only for illustrative purposes and are not to be construed in any way to limit the teaching hereof.

EXAMPLES

Synthesis of HTBN

Examples describing the synthesis of HTBN by the process of the present invention and the physical properties of the so-formed HTBN are presented below, with a comparison of the physical properties of the commercial HTBN, "HYCAR" 1300X29.

The CTBN used was "HYCAR" 1300X31, commercially
available from B.F. Goodrich, which contains about 10% by
weight of acrylonitrile, has a nominal end functionality of
about 1.9 and a number average molecular weight (M_n) of
5   about 3,800 (as determined by vapor pressure osmometry).

Example 1

        To a 3-necked, 1 liter reaction flask equipped
with a mechanical stirrer, thermocouple and addition funnel
10 was introduced with stirring about 302.48 grams (about 0.08
moles) of CTBN. The CTBN was heated to a temperature of
about 125°C, at which temperature about 9.23 grams (about
0.33 moles) of ethylene carbonate and about 6.98 grams
(about 0.027 moles) of tetraethylammonium iodide were
15 introduced. The temperature of the reaction mixture was
then increased to about 135°C. After a period of time of
about 5 minutes, the mixture was observed to darken and
began to foam. Stirring and heating were continued for an
additional period of time of about 55 minutes, while
20 maintaining the reaction temperature within the range of
about 125 to about 135°C. The contents of the vessel were
then cooled to a temperature of about 50°C and poured, with
vigorous stirring, into a vessel containing about 1 liter of
methanol, at room temperature.
25   On standing, the crude reaction product settled to
the bottom of the vessel and the methanol was decanted. The
product was then washed twice with 500 ml portions of
methanol, with the methanol removed by decanting after each
washing. The product was then placed in a crystallizing
30 dish and heated to a temperature of about 80°C under a
vacuum and maintained under such conditions for a period of
time of about 11 hours. After such time, about 250 grams of
HTBN was recovered corresponding to a yield of about 83%.
        The structure of the HTBN product was confirmed by
35 spectral analyses as follows: 'H NMR (CDCl.): δ=3.83, m, 2H and
δ=4.23, m, 2H; terminal methylene group protons

-C(O)OCH$_2$CH$_2$OH; IR (KBr film): 3512 cm^{-1} (-OH); 2250 cm^{-1} (-CN); 1745 cm^{-1} (carbonyl group of ester).

In addition, the ^{1}H NMR spectrum of the HTBN product showed neither the starting reagents, ethylene carbonate and phase transfer catalyst, nor ethylene glycol, a potential hydrolysis by-product. Residual methanol from the purification step was also shown to have been removed. The spectral characteristics of the HTBN product obtained by this method were observed to be similar to those obtained from the "HYCAR" 1300X29 HTBN product.

Example 2

To a 3-necked, 500 ml reaction flask equipped with a mechanical stirrer, thermocouple and addition funnel was introduced with stirring about 159.22 grams (about 0.04 moles) of CTBN. In this case, the stirred CTBN was heated to a temperature of only about 80°C, at which temperature about 15.41 grams (about 0.18 moles) of ethylene carbonate was introduced. The temperature of the reaction mixture was then increased to about 140°C and thereafter about 3.68 grams (about 0.014 moles) of tetraethylammonium iodide was introduced. Almost immediately, gas bubbles were observed to form in the bulk mixture. Stirring and heating were continued for a period of time of about 45 minutes, while maintaining the reaction temperature within the range of about 140 to about 143°C. The contents of the flask were then cooled and about 500 ml of dichloromethane was introduced. The polymer solution so formed was transferred to a separator funnel and washed twice with about 500 ml portions of water. The organic layer was separated, dried over anhydrous sodium sulfate and then filtered.

The solution was then transferred to an evaporating dish and warmed to a temperature of about 45°C to remove most of the methylene chloride, and then heated to a temperature of about 60°C under vacuum for a period of time of about 8 hours to yield about 140.89 grams of HTBN corresponding to an about 89% recovery. The warm polymer

was then transferred to a distillation flask and heated on a rotary evaporator at a temperature of about 95°C for a period of time of about 3.5 hours under reduced pressure. The product obtained was found by NMR and IR analyses to be identical to the product described in Example 1.

Example 3

Example 1 supra was repeated using about equimolar amounts of CTBN and ethylene carbonate, the progress of which was monitored by NMR analysis (through the emergence of signals at $\delta=3.85$ and $\delta=4.23$) with a sampling frequency of about 0.5 hours. HTBN product was not detected until the reaction mixture had been heated for a period of time of about 1.5 hours. In contrast, when that reaction was performed with an about 2-fold molar excess of ethylene carbonate, substantially complete conversion of CTBN to HTBN was observed after a period of time of about 1 hour. This indicates that the reaction rate is significantly enhanced by employing excess ethylene carbonate.

Example 4

Example 1 supra was repeated with the temperature of the mixture being maintained in the range of about 100 to about 107°C throughout the heating period. NMR analysis indicated that no HTBN product had formed after a period of time of about 1 hour.

Example 5

Example 1 supra was again repeated with the temperature of the mixture being maintained in the range of about 155 to about 160°C throughout the heating period. ^{1}H NMR analysis indicated that the degree of hydroxyalkylation decreased from substantial completion to about 70% after a period of time of about 1.5 hours.

Example 6

To a 3-necked, 250 ml reaction flask, equipped with a mechanical stirrer, thermocouple temperature

SUBSTITUTE SHEET (RULE 26)

controller and addition funnel was added about 111.82 grams
(about 0.029 moles) of "HYCAR" CTBN 1300X31. The stirred
polymer was heated to a temperature of about 100°C, at which
temperature about 9.84 grams (about 0.11 moles) of ethylene
5   carbonate and about 0.608 grams of *p*-toluenesulfonic acid
were added. The temperature of the mixture was increased
over the course of about 5 minutes and when the temperature
reached about 120°C the mixture darkened in color and began
to foam. The temperature of the reaction mixture was
10   allowed to increase thereafter to about 132°C over the
course of about 15 minutes. Stirring and heating were
continued for an additional period of time of about 0.5
hours while maintaining the reaction temperature between
about 132 and 137°C. ^{1}H NMR analysis indicated that HTBN
15   product was not present in the crude reaction mixture after
that time.

Example 7
             To a 3-necked, 5-liter resin kettle equipped with
20   a mechanical stirrer and thermocouple was added about 1570
grams (about 0.39 moles) of "HYCAR" 1300X31 CTBN. The
stirred polymer was heated to a temperature of about 115°C,
at which temperature about 152 grams (about 1.7 moles) of
ethylene carbonate and about 36 grams (about 0.14 moles) of
25   tetraethylammonium iodide as a phase transfer catalyst were
added. The mixture was observed to darken in color and
thereafter begin to foam.
             The temperature of the mixture was increased to
about 135°C, with continued stirring and heating for a total
30   period of time of about one hour while maintaining the
reaction temperature in the range of about 134 to about
136°C. The contents of the kettle were cooled to a
temperature of about 70°C and about 47.2 grams of magnesium
silicate ("MAGNESOL" Polysorb 30/40) were added, with
35   stirring continued for a period of time of about 3 hours.
After such time, about 15.8 grams of the filtration aid
"CELITE" 503 were added, with stirring for another 15
minutes then filtered at a pressure of about 41 psi and a

SUBSTITUTE SHEET (RULE 26)

temperature of about 66°C through a filter having a pore
size of 25μ. ¹H NMR spectrum of the filtered material
showed that catalyst was absent. Ethylene carbonate was
removed by wiped-film evaporation under reduced pressure to
5   yield HTBN, having spectral characteristics similar to the
product prepared in Example 1. Analyses showed the material
to have an hydroxyl number of 23 and a carboxyl number of
less than about 0.1.

10   Example 8

    To a 3-necked, 5 liter resin kettle equipped with
a mechanical stirrer, thermocouple and addition funnel was
added with stirring about 1,604.11 grams (about 0.42 moles)
of "HYCAR" CTBN 1300X31. The stirred polymer was heated to
15   a temperature of about 110°C, at which temperature about
155.28 grams (about 1.76 moles) of ethylene carbonate and
about 37.15 grams (0.14 moles) of tetraethylammonium iodide
as the phase transfer catalyst were added. The temperature
of the mixture was increased to about 126°C, and stirring
20   and heating were continued for an additional period of time
of about 175 minutes while maintaining the reaction
temperature in the range of about 121 to about 128°C.

    The contents of the reactor were cooled to about
60°C and about 49 grams of magnesium silicate ("MAGNASOL"
25   Polysorb 30/40) was added. The mixture was stirred for a
period of time of about 4 hours and centrifuged for a period
of time of about 10 minutes at a rate of about 2,500 rpm to
separate the silicate. ¹H NMR analysis indicated that
substantially all of the phase transfer catalyst was removed
30   as indicated by the disappearance of the characteristic
methylene proton signal at $\delta=3.48$.

    A small aliquot (about 2 grams) of the centrifuged
material was heated to a temperature of about 80°C under
vacuum for a period of time of about 7 hours to provide
35   HTBN, substantially free of ethylene carbonate, having the
spectral characteristics of the HTBN product prepared in
accordance with Example 1.

Example 9

Carboxylic acid-functionalized materials other
than HTBN were treated with hydroxyalkylating agents in
accordance with the process of the present invention to
5   yield corresponding hydroxyl-functionalized materials.

For instance, we treated trans-3-hexenoic acid (a
low molar mass model compound for HTBN) with ethylene
carbonate in the presence of a phase transfer catalyst to
yield 2-hydroxyethyl-3-hexenoate. More specifically,
10   trans-3-hexenoic acid (about 1.14 grams; about 0.001 moles,
commercially available from Aldrich Chemical Co., Milwaukee,
Wisconsin), ethylene carbonate (about 0.97 grams; about
0.001 moles) and phase transfer catalyst were added to a 25
ml reaction flask containing a magnetic stirrer. The
15   mixture was stirred at elevated temperature conditions to
effect the hydroxyethylation reaction of the hexenoic acid.
The reaction yields were estimated from the ^{1}H NMR spectrum
of the crude product mixture.

The results obtained for a variety of parameter
20   variations (such as, identity and quantity of phase transfer
catalyst, time and temperature of the reaction, and the
like) are presented below in Table 1.

25

30

35

Table 1

Catalyst	Equivalents conc.	Temp. (°C)	Time (hours)	Yield (%)
none	--	150	2	0
Potassium carbonate	0.35	150	2	0
Tetrabutyl ammonium bromide	0.05	135	5	61
Tetrabutyl ammonium bromide	0.1	130	3	76
Tetrabutyl ammonium bromide	0.2	140	1	92
Tetrabutyl ammonium bromide	0.1	135	10	0
Tetraethyl ammonium iodide	0.2	140	0.33	51
Tetraethyl ammonium iodide	0.2	140	0.66	63
Tetraethyl ammonium iodide	0.2	140	1	77

Example 10
Evaluation of HTBN

Molecular Weight Determination

Initially, we measured the molecular weight of the HTBN formed in Examples 1 and 2 supra using size exclusion chromatography employing a high pressure liquid chromatography system [Styragel HR 5 μ column set (commercially available from Waters, Incorporated), with pore sizes 10^6, 10^4 and 500 Å], equipped with a differential refractometer. The system was calibrated with conventional polystyrene standards. Tetrahydrofuran was used as a mobile phase at a flow rate of about 1 ml/min.

We examined refractometer measurements of the eluted fractions and determined the molecular weight to be about 10,100 for the commercial HTBN compared to about

SUBSTITUTE SHEET (RULE 26)

10,400 and about 11,300 for the HTBN products derived from
ethylene carbonate in Examples 1 and 2, respectively.
Molecular weight distributions were found to be about 1.8
for each material. Thus, good agreement was found in this
5   regard between the HTBN prepared by the process of the
present invention and the commercial HTBN.

Hydroxyl Number

        We also determined the hydroxyl number for HTBN
10   prepared by the process of the present invention and its
commercial counterpart. The hydroxyl number is a measure of
the concentration of hydroxyl groups on the polymeric
structure and is desirable to ensure that the stoichiometric
equivalent of diisocyanate be employed in the production of
15   the block-prepolymer intermediate. Hydroxyl numbers were
determined here by standard titration techniques and are
reported here as mg of KOH/g of polymer.
        We found the commercial HTBN to possess an
hydroxyl number of 22.7 and the HTBN prepared from ethylene
20   carbonate in Examples 1 and 2 supra to possess an hydroxyl
number of 22.2 and 21.4.

Acid Numbers

        The acid number is the amount of free carboxylic
25   acid and is used to determine residual unreacted carboxylic
acid at the completion of the reaction. It is desirable for
the HTBN to have a low acid number, particularly when the
HTBN is to be used to prepare urethane resins, because acid
functionalized polymers (e.g., CTBN) react only slowly and
30   incompletely with isocyanates. We found the process of the
present invention to provide materials essentially free of
carboxylic acid functionality, which compares favorably with
values obtained from commercial HTBN.
        In order to determine the acid number of the HTBN,
35   we used standard titration techniques and reported the acid
values as mg of KOH/g of polymer. The HTBN prepared by the
process of the present invention exhibited an acid number of
less than 0.1, whereas the commercial HTBN exhibited an acid

number of about 2.6. Thus, it is seen that with respect to
acid conversion, the process of the present invention
provides greater than a twenty fold decrease in residual
acid, which results in a cleaner urethane product and is
5   desirable to ensure that the stoichiometric equivalent of
diisocyanate be employed in the production of the
block-prepolymer intermediate.

Presence of Residual Glycol

10   ^{1}H NMR analysis of commercial HTBN showed the
presence of ethylene glycol in an amount in the range of
about 0.29 to about 0.43 by weight percent. The presence of
ethylene glycol in HTBN prepared from CTBN and excess
ethylene oxide is not entirely surprising as residual
15   ethylene oxide may be converted to ethylene glycol by
hydrolysis. However, the presence of ethylene glycol in the
HTBN is disadvantageous for certain applications to the
extent that it reduces the toughness of block resins derived
from HTBN. While this attribute may be beneficial in
20   certain applications, in other applications where enhanced
stiffness or reactivity is required, it is desirable to have
the choice of whether or not a less tough material is to be
formed. That is, in the event that a less tough
HTBN-derived block resin is desirable for certain
25   applications, ethylene glycol could nevertheless be added to
the HTBN. With the process of the present invention, no
ethylene glycol is produced and thus a tougher HTBN-derived
block resin is afforded.

30   ### Miscellaneous
         Of course, since the process of the present
invention does not call for a trialkyl amine coreactant,
residual amine is ordinarily zero or at most minimal.
Again, we used standard titation techniques to determine the
35   presence of amine, which is reported as mg of KOH/g of
polymer. The amine value for commercial HTBN was determined
to be about 1.19, whereas the amine value for an HTBN
prepared according to the present invention was determined

to be about 0.19. It is desirable to have a low amine value
because amines contribute to variable reactivity and product
instability during the preparation of the block-prepolymers.

5   <u>Synthesis of Block Resins</u>

We prepared block resins in accordance with the
teaching of the '909 patent from both HTBN prepared using
the process of the present invention and commercially
available HTBN, and thereafter evaluated the properties and
10 characteristics of the resulting block resins. Those
results are described below.

<u>Example 11</u>

Block resins were prepared from HTBN prepared by
15 the process of the present invention as follows.

To a 3-necked, 500 ml reaction flask equipped with
a mechanical stirrer, thermocouple and condenser/inlet port
was introduced with stirring about 7 grams (about 0.029
moles) of hydrogenated bisphenol-A ("HBPA"), about 48.06
20 grams (about 0.168 moles) of triethyleneglycol
dimethacrylate, about 0.27 grams (about 0.72 mmoles) of
dibutyltin dilaurate, 0.04 grams (about 0.37 mmoles) of
benzoquinone and about 0.96 grams (about 0.01 moles) of
methacrylic acid.

25 The mixture was heated to a temperature of about
70°C under a nitrogen atmosphere for a period of about 0.5
hours, and about 10.17 grams (about 0.058 moles) of toluene
diisocyanate ("TDI") (80% 2,4- and 20% 2,6 isomers) was
introduced dropwise over a period of time of about 2
30 minutes. Thereafter, a reaction exotherm was observed,
during which the temperature increased to about 83°C and the
mixture was observed to clarify. Heating and stirring were
continued for a further period of time of about 1 hour,
after which time about 56.34 grams (about 0.015 moles) of
35 HTBN, prepared as described above in Example 1 <u>supra</u>, was
introduced. Heating and stirring were continued for a
further period of time of about 2 hours, at which time about
2.98 grams (about 0.028 moles) of 2-hydroxyethyl

SUBSTITUTE SHEET (RULE 26)

methacrylate ("HEMA") and about 0.14 grams (about 0.37
mmoles) of dibutyltin dilaurate were introduced. Heating
and stirring were continued for an additional period of time
of about 6 hours, after which time an IR spectrum of the

5   reaction mixture indicated that all of the isocyanate was
consumed (through the disappearance of the absorption band
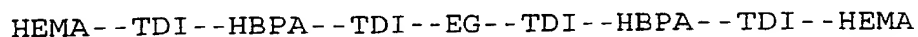of the isocyanate at 2265 cm^{-1}).

The reaction mixture was cooled and spectral and
chromatographic analysis confirmed the cooled product to be

10   a methacrylate-terminated urethane block co-polymer having a
flexible HTBN derived center segment and rigid urethane end
segments similar to the product described in Example 1 of
the '909 patent, having the following structure:

15   HEMA--TDI--HBPA--TDI--HTBN--TDI--HBPA--TDI--HEMA

where each urethane group is indicated by the dashed line
(--). This block resin is referred to hereinafter as Resin
A. Size exclusion chromatography as described supra showed

20   Resin A to have a number average molecular weight of about
19,500

Example 12

For comparative purposes, block resins were

25   prepared from commercially available "HYCAR" 1300X29 HTBN.
Since the "HYCAR" HTBN polymer contains a significant
concentration of ethylene glycol, block resins prepared with
that HTBN can be expected to contain, in addition to the
resin above, a short rigid block derived from an ethylene

30   glycol ("EG") center segment, having the following
structure:

           HEMA--TDI--HBPA--TDI--EG--TDI--HBPA--TDI--HEMA

35   The difference in structure representation is seen to be due
to the similarity in reactivity of isocyanate with either
Resin A and the block resin whose structure is depicted
above (referred to hereinafter as Resin B).

SUBSTITUTE SHEET (RULE 26)

With respect to the production of block resins
through an isocyanate/polyol addition, while the presence of
ethylene glycol may be advantageous for certain applications
it is disadvantageous for the purpose of preparing toughened

5   block resins. In this regard, ethylene glycol has
substantially equivalent reactivity to the HTBN resin and
results in the formation of a short, and hence rigid,
urethane oligomer which in turn results in adhesive products
with reduced toughness. Further, if the concentration of

10   the ethylene glycol varies, then adhesive products with
variable rheological and mechanical properties will be
produced. Such variations is often viewed as unacceptable.

Example 13

15   Evaluation of Properties of Block Resins
Molecular Weight Determination
We measured the molecular weight of the block
resins as so prepared in this example using size exclusion
chromatography and the protocol set forth above with respect

20   to the HTBN materials. The number average molecular weight
of Resin A was determined to be about 19,500. In contrast,
the number average molecular weight of Resin B was
determined to be about 18,000.
As the molecular weight of the EG prepolymer is

25   significantly lower than that of the HTBN material, it is to
be expected that the molecular weight of a blend of the EG
and HTBN products will be lower than that of the HTBN formed
in accordance with this invention, such as the HTBN used to
prepare Resin A.

30   Thus, block resins prepared from the HTBN formed
in accordance with the process of this invention (i.e.,
Resin A) demonstrated a higher number average molecular
weight due, in part, to lower levels of short blocks derived
from ethylene glycol, which are present in Resin B. This

35   difference may provide further opportunities for block
resins prepared from HTBN formed in accordance with this
invention, such as where improved thoughness and elongation

are desirable properties to extend the range of applications
for adhesives, protective coatings and sealant compositions.

Example 14

5   Curing of Block Resins

We cured the block resins prepared as described in
Examples 11 and 12 supra by dissolving therein about 1% by
weight of the UV/visible photoinitiator "IRGACURE" 1700 [the
combination of about 25% bis-(2,6-dimethoxybenzoyl)-
10   2,4-,4-trimethylpentyl phosphine oxide and about 75%
2-hydroxy-2-methyl-1-phenyl-propan-1-one, commercially
available from Ciba-Geigy Corporation, Tarrytown, New York].

Each of the photoinitiator-containing block resins
was applied between glass/polyester plates and cured by
15   exposure to ultraviolet light, emitted from a Fusion Systems
conveyer assembly equipped with a "D" bulb and reflectors,
at a fluence of 1 J/cm^2/side. The resins cured to a film
having a thickness of about 0.5 mm.

20   Example 15

Evaluation of Properties of Cured Block Resins

We evaluated the physical properties and
characteristics of the resulting reaction product of the
cured block resins, a summary of which is provided below.

25   The mechanical properties of the cured films were
determined from (1) stress-strain measurements using an
Instron universal tensile tester operating at a strain rate
of about 0.2"/min., with a film size of about 101.6 X 6.35
mm^2 and (2) dynamic mechanical analysis ("DMA") using a
30   Rheometrics Analyzer II in oscillatory shear strain
operating at a frequency of about 10 radians/sec., with a
film size of about 25 X 12 mm^2. The results are presented
below in Table 2:

35

-33-

Table 2

PHYSICAL PROPERTY	CURED RESIN	
	A	B
MODULUS (PSI)	54,260	56,780
STRESS AT BREAK (PSI)	2,561	2,527
STRAIN AT BREAK (PSI)	63	39
TOUGHNESS (in.lbs./cm^3)	1,206	790
T_g1 (°C)	-55.5	-55.7
tanδ1	0.12	0.11
T_g2 (°C)	93	112
tanδ2	0.24	0.20

The tabulated results show that the two cured
block resins have similar stiffness and breaking strength.
However, the elongation at break and toughness of cured
Resin A are superior to that of cured Resin B.

More specifically, both cured resins show two
distinct transitions in the DMA spectrum, a low temperature
transition, designated T_g1, and a high temperature
transition, designated T_g2. The two transitions are
indicative of a two-phase morphology. The similarity of the
DMA parameters (T_g, tan values) indicates a similar
structure for the cured resins. The low temperature
transition (at about -55°C) occurs at about the same
temperature for both of the cured resins and is associated
with the rubbery central segment derived from HTBN. The
high temperature transition (at about +100°C) is associated
with the stiffer urethane end segments and is lower for
cured Resin A than for cured Resin B. The lower T_g2 value
for cured Resin A may be attributed to the absence of
ethylene glycol in the HTBN prepared by the process of the
present invention (and hence the absence of the

SUBSTITUTE SHEET (RULE 26)

corresponding rigid short chain urethane oligomer present in Resin B). This result correlates well with the increased toughness associated with cured Resin A.

^{1}H NMR analysis indicated the presence of ethylene glycol (about 0.5% by weight, about 24 mole percent) in the HTBN prepared in accordance with the '691 patent, or commercial HTBN. While minor in terms of weight inclusion, the presence of ethylene glycol represents a significant concentration in molar terms, to the large disparity in molecular weight between ethylene glycol and HTBN. If the hydroxyl number determined for the commercial HTBN polymer is adjusted by subtracting the estimated contribution due to ethylene glycol, the hydroxyl value attributable to the HTBN is reduced from 25.3 to 19.5. Thus, the hydroxyl number for HTBN prepared in accordance with this invention is at least comparable, if not slightly higher, than that of the commercial HTBN. Ethylene glycol was not detected in the HTBN prepared in accordance with this invention.

Amine analysis also indicated the presence of residual amine in the commercial HTBN product. This amine impurity is known to cause premature polymerization and formation of urethane/isocyanate by-products, particularly when (meth)acrylate capping reagents and diluents are employed with respect to the production of urethane prepolymers. Accordingly, it is desirable and advantageous to first remove or neutralize the amine catalyst, prior to the introduction of isocyanate monomers.
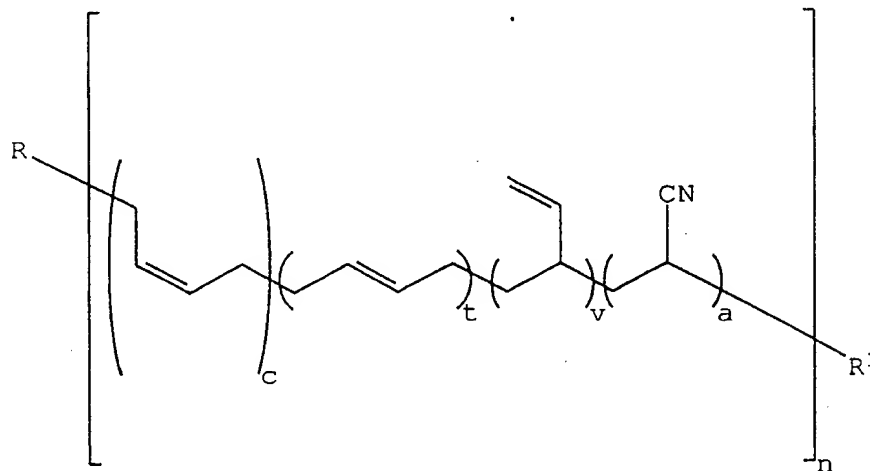
The HTBN prepared in accordance with this invention is also substantially free of carboxylic acid functionalized materials. Carboxylic acids are undesirable, since they are known to compete with hydroxyl groups for isocyanate and result in the formation of complex mixtures of ureas, anhydrides, amides and carbon dioxide.

The scope of the present invention may be gleaned from the claims.

SUBSTITUTE SHEET (RULE 26)

<u>What is Claimed Is</u>:

1.   A process for preparing an hydroxyl-functionalized material, said process comprising the step of:

reacting as reactants (a) a carboxylic acid-functionalized material represented by:

wherein R and R^1 may be the same or different and may be selected from COOH or CAA^1-X-COOH, A and A^1 may be the same or different and may be selected from hydrogen, halogen, cyano or linear or branched alkyl groups having from 1 to about 5 carbon atoms and X may be selected from linear or branched alkyl groups having from 2 to about 5 carbon atoms, c+t+v+a=1, and n is an integer in the range of from about 5 to about 750, with (b) an hydroxyalkylating reagent selected from the group consisting of carbocyclic carbonates and carbocyclic sulfites, in the presence of (c) a phase transfer catalyst, under conditions sufficient to form the hydroxyl-functionalized material.

2.   The process according to Claim 1, wherein said carboxylic acid-functionalized material is selected from the group consisting of the following carboxylic acid-functionalized polymers: polyethylene, polybutadiene, polyisoprene, poly(butadiene-co-acrylonitrile), poly(isobutylene), poly-(butadiene-co-styrene),

SUBSTITUTE SHEET (RULE 26)

poly(butadiene-co-acrylonitrile-co-acrylic acid), poly(ethyl
acrylate), poly(ethyl acrylate-co-n-butyl acrylate),
poly(n-butyl acrylate-co-acrylonitrile), poly(butyl
acrylate-co-styrene), and combinations thereof.

3.   The process according to Claim 1, wherein
said hydroxyalkylating reactant is a member selected from
the group consisting of carbocyclic carbonate, carbocylic
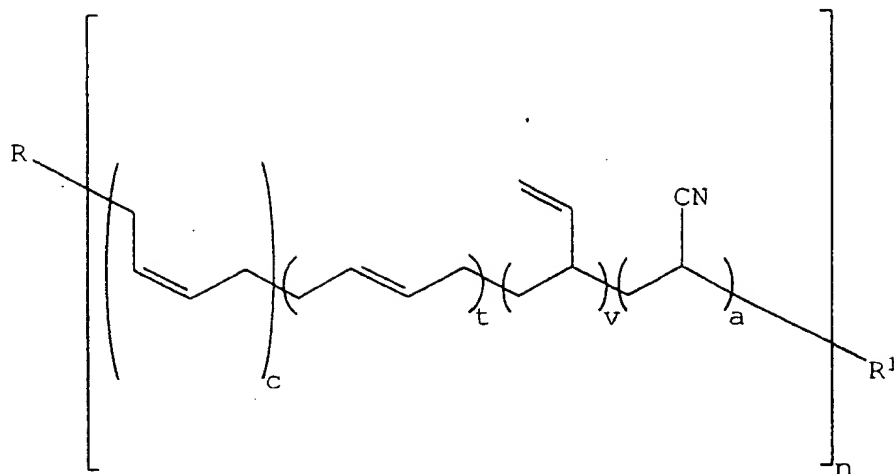sulfites and combinations thereof.

4.   The process according to Claim 3, wherein
said carbocyclic carbonate is a member selected from the
group consisting of ethylene carbonate, 1,3-propylene
carbonate, 2-methyl-1,2-ethylene carbonate,
3-methyl-1,3-propylene carbonate, 1,2-dimethyl methylene
carbonate, 2,2-dimethyl butylene carbonate and combinations
thereof.

5.   The process according to Claim 3, wherein
said carbocyclic carbonate is ethylene carbonate.

6.   The process according to Claim 3, wherein
said carbocyclic sulfite is a member selected from the group
consisting of ethylene sulfite, propylene sulfites and
combinations thereof.

7.   The process according to Claim 3, wherein
said carbocyclic sulfite is ethylene sulfite.

8.   The process according to Claim 1, wherein
said hydroxyl-functionalized material is represented by:

$$\left[R \left(\begin{array}{c} \\ \\ \end{array} \right)_c \left(\begin{array}{c} \\ \\ \end{array} \right)_t \left(\begin{array}{c} CN \\ \\ \end{array} \right)_v \left(\begin{array}{c} \\ \\ \end{array} \right)_a R^1 \right]_n$$

wherein R and R^1 may be the same or different and may be selected from COO-X'-OH or CAA'-X-COO-X'-COOH, wherein A and A' may be the same or different and may be selected from hydrogen, halogen, cyano or linear or branched alkyl groups having from 1 to about 5 carbon atoms, and X and X' may be the same or different and may be selected from linear or branched alkyl groups having from 2 to about 5 carbon atoms, c+t+v+a=1 and n is an integer in the range of from about 5 to about 750.

9.   The process according to Claim 1, wherein said hydroxyl-functionalized material is selected from the group consisting of the following hydroxyl-functionalized polymers: polyethylene, polybutadiene, polyisoprene, poly(isobutylene), poly(butadiene-co-acrylonitrile), poly(butadiene-co-styrene), poly(butadiene-co-acrylonitrile-co-acrylic acid), poly(ethyl acrylate), poly(ethyl acrylate-co-n-butyl acrylate), poly(n-butyl acrylate-co-acrylonitrile), poly(butyl acrylate-co-styrene), and combinations thereof.

10.   The process according to Claim 1, further comprising the step of providing an amphoteric treating agent in an amount sufficient to cause the

SUBSTITUTE SHEET (RULE 26)

hydroxyl-functionalized material to separate from the reactants which remain and/or any by-products thereof.

11. The process according to Claim 10, wherein the amphoteric treating agent is a member selected from the group consisting of silicated magnesium oxide, magnesium oxide, magnesium hydroxide, calcium hydroxide, barium oxide, barium hydroxide and combinations thereof.

12. The process according to Claim 1, wherein the phase transfer catalyst is a member selected from the group consisting of quaternary ammonium halides, phosphonium halides, sulfonium halides, crown ethers, calixarenes and combinations thereof.

13. The process according to Claim 1, wherein the phase transfer catalyst is a member selected from the group consisting of tetrabutyl ammonium iodide, tetraethyl ammonium iodide, benzyl trimethyl ammonium chloride and ethyl triphenylphosphonium bromide.

14. The process according to Claim 1, wherein the amount of hydroxyalkylating reagent is 3 to 10 parts by weight of the carboxylic acid-functionalized material.

15. The process according to Claim 1, wherein the carboxylic acid-functionalized material is a member selected from the group consisting of carboxylic acid-functionalized polybutadiene and carboxylic acid-functionalized poly(butadiene-co-acrylonitrile).

16. Hydroxyl-functionalized materials prepared by the process according to Claim 1.

17. An adhesive, coating or sealant composition having improved toughness and elongation properties and curable through a gap of more than 40 mils, said composition comprising (a) a reaction product of (i) the

hydroxyl-functionalized material according to Claim 1, and
(ii) a molar excess of a reaction product of a molar excess
of an aromatic or cycloaliphitic polyisocyanate and a
compound selected from the group consisting of an aromatic
or cycloaliphatic polyol, the reaction product of (i) and
(ii) subsequently being reacted with a molar excess of a
compound selected form the group consisting of a
hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an amino
alkyl acrylate, an amino alkyl methacrylate and combinations
thereof; and (b) an initiator selected from the group
consisting of free radical initiators and photo-initiators.

18.   The composition according to Claim 17,
wherein the polyisocyante is a member selected from the
group consisting of toluene diisocyanate and
4,4'-diisocyanate diphenyl methane; and the reaction product
in (a) is an isocyantate-terminated hydrogenated bisphenol-A
and toluene diisocyanate.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07C 67/24, 69/82; C08F 8/00, 8/14; C08G 63/42

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/123, 328.8, 329.2, 329.3, 3343, 348, 383; 528/272, 285, 296, 298, 307, 308, 309; 560/84, 85, 86, 89, 127, 193, 194, 198

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,266,046 A (WU) 05 May 1981, see abstract.	1-18
A	US 4,310,707 A (STREGE) 12 January 1982.	1-18
A	US 4,513,146 A (THOMPSON) 23 April 1985.	1-18
A	US 5,019,629 A (WOODS et al) 28 May 1991.	1-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 APRIL 1998	26 MAY 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BERNARD LIPMAN Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

525/123, 328.8, 329.2, 329.3, 3343, 348, 383; 528/272, 285, 296, 298, 307, 308, 309; 560/84, 85, 86, 89, 127, 193, 194, 198

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)1-16, drawn to a process of hydroxylation.
Group II, claim(s) 17 and 18, drawn to adhesive compositions.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the adhesives of Group II do not rely on the technical features of the process of Group I, since the hydroxylated materials of the adhesives could be made by different process.

United States Patent [19]

Pohl

[11] **4,137,081**

[45] **Jan. 30, 1979**

[54] **PRINTING PLATES FROM POLYMER WITH TERMINAL UNSATURATION**

[75] Inventor: Rudolph L. Pohl, Newark, Del.

[73] Assignee: Hercules Incorporated, Wilmington, Del.

[21] Appl. No.: 810,334

[22] Filed: Jun. 27, 1977

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 628,862, Nov. 5, 1975, abandoned.

[51] Int. Cl.^{2} G03C 1/78; G03C 1/96; G03C 1/68; G03C 5/00
[52] U.S. Cl. .... 96/87 R; 96/35.1; 96/36.3; 96/86 P; 96/115 R; 96/115 P; 204/159.15; 204/159.16
[58] Field of Search .... 96/35, 35.1, 36.3, 86 P, 96/115 R, 115 P, 87 R; 204/159.24, 159.15, 159.16

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,467,523	9/1969	Seidel et al.	96/115 R
3,628,963	12/1971	Akamatsu et al.	96/115 R
3,787,212	1/1974	Heimsch et al.	96/35.1
3,809,633	5/1974	Magnotta et al.	204/159.14
3,861,917	1/1975	Magnotta et al.	96/86 P X
3,907,574	9/1975	Yonezawa et al.	204/159.15 X
3,929,489	12/1975	Arcesi et al.	204/159.15 X

Primary Examiner—Edward C. Kimlin
Attorney, Agent, or Firm—Marion C. Staves

[57] **ABSTRACT**

It has been found that excellent quality photopolymer printing plates having hardness, flexibility, resilience, abrasion resistance and resistance to alcohol-based inks can be prepared from photopolymer compositions comprising a liquid polymer containing at least two terminal olefin groups attached to the polymer through a combination of at least two ether, thioether, ester, keto or amide groups, from about 1 to about 50% by weight based on the polymer of at least one ethylenically unsaturated monomer, from about 0.1 to about 10% by weight of a photoinitiator and about 0.01 to about 2% of a stabilizer.

10 Claims, No Drawings

1

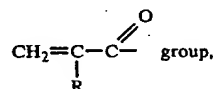### PRINTING PLATES FROM POLYMER WITH TERMINAL UNSATURATION

This application is a continuation-in-part of my copending U.S. application Ser. No. 628,862 filed Nov. 5, 1975, now abandoned.

This invention relates to photopolymer compositions, processes for making printing reliefs and to photopolymer elements. More particularly, this invention relates to liquid, water dispersible photopolymer compositions which on exposure to actinic radiation will give crosslinked structures having hardness, flexibility, resilience, abrasion resistance and resistance to alcohol-based inks; photopolymer plates embodying a layer of such composition; and the process of making printing plate reliefs from such compositions.

Compositions capable of being converted under the influence of actinic light to solid, insoluble, tough structures are well-known and have become increasingly important in the preparation of printing plates. One of the fundamental patents relating to such compositions is U.S. Pat. No. 2,760,863 to Plambeck. In the process of the Plambeck patent, printing plates are produced directly by exposing to actinic light through an image-bearing process transparency a layer of an essentially transparent composition containing an addition polymerizable, ethylenically unsaturated monomer and an additional polymerization initiator activatable by actinic light. The layer of polymerizable composition is supported on a suitable support, and exposure of the composition is continued until substantial polymerization of the composition has occurred in the exposed areas with substantially no polymerization occurring in the nonexposed areas. The unchanged material in the latter areas then is removed, as by treatment with a suitable solvent in which the polymerized composition in the exposed areas is insoluble. This results in a raised relief image which corresponds to the transparent image of the transparency and which is suitable for use as a printing plate, as in letterpress and dry off-set work.

Photopolymerizable layers of the type of the Plambeck patent generally are prepared from polymeric components which are soluble in organic solvents. Accordingly, development of printing plates based on such compositions has required the use of organic solvents or of solutions containing high percentages of organic solvents. Due to the toxicity, high volatility and generally low flash point of low cost organic solvents, their use often gave rise to hazardous conditions. As a consequence, further research was directed and led to the development of several photopolymer layers which are soluble in water or aqueous alkali. For example, these layers have utilized polymeric components containing lateral acid groups, or the soluble salts thereof or certain water-soluble polymer compositions. In U.S. Pat. No. 3,794,494 water or aqueous alkali dispersible compositions are described suitable for use in rigid or elastic flexographic printing plate preparation. These compositions comprise combinations of unsaturated polyesters, polyunsaturated monomers and a photopolymerization initiator. However, flexible printing plates suitable for use in flexographic printing using alcohol-based inks cannot be prepared using compositions of the type described in the patent because the quick drying alcohol-based inks used in flexographic printing will cause the cured compositions to swell and disintegrate.

2

It has now been discovered that excellent quality photopolymer printing plates having hardness, flexibility, resilience, abrasion resistance and resistance to alcohol-based inks can be prepared from certain unique photopolymer compositions in accordance with this invention. The photopolymer composition of this invention comprises (1) a liquid polymer containing at least two terminal olefin groups attached to the polymer through a combination of at least two ether, thioether, ester, keto, or amide groups, (2) from about 1 to about 50% by weight based on the liquid polymer of at least one ethylenically unsaturated monomer selected from the group consisting of acrylonitrile, styrene, methyl substituted styrenes, N-vinyl pyrrolidone, and a monomer having its unsaturation in the form of at least one

$$CH_2=C-C\overset{O}{\underset{R}{\overset{\parallel}{{}}}}- \quad group,$$

wherein R is hydrogen or a C_1-C_3 alkyl group, (3) from about 0.1 to about 10% by weight of a photoinitiator, and (4) about 0.01 to about 2% of a thermal polymerization inhibitor.

While the photopolymer compositions of this invention are not water-soluble, they are sufficiently water-dispersible so that unexposed portions of printing plates prepared from said compositions can be removed by washing with dilute aqueous solutions of a detergent. Particularly useful detergents are anionic detergents such as olefin sulfonates.

The photopolymer compositions of this invention can readily be applied to a support, such as for example polyester film or a grained-metal sheet, from solution or by conventional coating procedures. Such layers will generally be from 3 to 250 mils in thickness. After exposure through a process transparency, the compositions are readily developable with an aqueous detergent solution to form printing reliefs, thus obviating the need for organic solvents, although organic solvents may be used either alone or in combination with water, if desired.

EXAMPLE 1

This example illustrates the use of a liquid polymer prepared from carboxyl terminated polybutadiene and glycidyl methacrylate, in a photopolymer composition in accordance with this invention.

Into a round bottom flask fitted with a stirrer, a reflux condenser, and an air sparge tube, is charged 3272 parts of a carboxyl terminated polybutadiene (sold by B. F. Goodrich Co. under the trademark "Hycar CTB"-2000X162) and 2.61 parts of sodium methoxide catalyst. The mixture is heated with stirring while a stream of dry air is passed through. When the temperature reaches 100° C., 229 parts of glycidyl methacrylate are added, along with a mixture of thermal stabilizers comprising 0.26 part nitrobenzene, 0.49 part phenothiazine and 6.55 parts of di-tert-butyl-para-cresol. The reaction mixture is maintained at a temperature of 100° C. for 11 hours. The resulting terminally unsaturated polymer has an acid number of 2.8 and a Brookfield viscosity measured at 25° C. of 92,410 cps.

A portion of the above prepared polymer, comprising 3087 parts, is stirred together with a mixture of unsaturated monomers comprising 210.5 parts of 1,6-hexanediol dimethacrylate and 210.5 parts of lauryl meth-

acrylate and 140.3 parts of 2,2-diethoxyacetophenone photoinitiator. This mixture is stirred at room temperature for 1 hour, at which time it is completely homogeneous. The resulting photopolymer composition has a Brookfield viscosity measured at 25° C. of 21,200 cps.

The above prepared photopolymer composition is then poured into a rubber frame 2 mm. thick. A glass plate is placed over the frame in contact with the composition. The composition is then exposed through the glass plate at room temperature for 60 seconds to a bank of 10 30-watt ultraviolet fluorescent lights (Westinghouse F30T8/BL) set at a distance of 7 cm. from the glass. The glass plate with the photopolymer composition attached is separated from the mold and immersed in a wash bath containing an aqueous solution of 1.0% α-olefin sulfonate detergent (sold by Stepan Chemical Corporation under the trademark "Bioterg"). The uncrosslinked liquid composition is dispersed in the aqueous solution. The portion of composition next to the glass (nearest the ultraviolet lights) is hardened. The thus hardened composition is peeled from the glass and dried. It is found to have a thickness of 0.014 inch.

EXAMPLE 2

This example illustrates the physical properties of the cross-linked photopolymer composition described in Example 1.

A sample of the photopolymer composition described in Example 1 is spread to a thickness of 0.04 inch on a glass plate using a doctor blade. The composition is covered with a 0.004 inch polyester film and exposed to ultraviolet lights as described in Example 1 for 20 seconds through the polyester film. The composition is then exposed through the glass plate to a 3 kilowatt medium pressure mercury arc lamp for 4.5 minutes. The polyester film is peeled off the cross-linked composition and the hardened composition in turn peeled off the glass. Dumbbell shaped samples are cut from the cross-linked composition and used to determine its physical properties. The cross-linked composition has a tensile strength of 240 psi, an elongation of 70%, a tensile modulus of 470 psi, a Bayshore resilience of 47%, and a Shore A hardness of 52.

EXAMPLE 3

This example illustrates the solvent resistant properties of the cross-linked photopolymer composition described in Example 1 in various solvents.

Samples of cross-linked photopolymer composition are prepared in a thickness of 50 mils as described in Example 2 and tested in various solvents. The percent weight gain and change in Shore A hardness are tabulated in Table I below:

TABLE I

SOLVENT RESISTANCE OF CROSS-LINKED PHOTOPOLYMER COMPOSITION

Run	Solvent	% Weight Gain (x)	Change in Shore A Hardness
a	Water	0	+2
b	Methanol	2	0
c	Ethanol	2	0
d	N-propanol	4	−2
e	Isopropanol	3	−2
f	Ethylene glycol	−1	+1
g	Propylene glycol	−1	+1
h	Diethylene glycol	−1	0
i	Cellosolve	10	−7
j	Butyl cellosolve	13	−1.4
k	Acetone	20	−3
l	Methyl Ethyl Ketone	50	−4

TABLE I-continued

SOLVENT RESISTANCE OF CROSS-LINKED PHOTOPOLYMER COMPOSITION

Run	Solvent	% Weight Gain (x)	Change in Shore A Hardness
m	Ethyl acetate	62	−4
n	Heptane	75	-disintegrated
o	Kerosene	82	−4
p	Xylene	—	-disintegrated
q	Perchloroethylene	—	-disintegrated
r	90% Denatured ethyl alcohol 10% Ethyl acetate	5	−2
s	80% Denatured ethyl alcohol 20% Ethyl acetate	9	−5
t	77% Water 17% Isopropanol 6% NH₄OH·Conc.	1.5	1.5

(x) After 24 hours immersion in solvent at room temperature, samples 59 mils thick, polyester substrate sheet attached.

EXAMPLE 4

This example illustrates the use of a liquid polymer prepared from carboxyl terminated butadiene-acrylonitrile copolymer and glycidyl methacrylate, in a photopolymer composition in accordance with this invention.

Into a flask equipped as described in Example 1 is charged 536 parts of a carboxyl terminated butadiene-acrylonitrile copolymer, having an acid number of 31.1 and containing 17% acrylonitrile, 98.0 parts of glycidyl methacrylate, 0.43 parts of sodium methoxide catalyst and 2.41 parts of di-tert-butyl-para-cresol stabilizer. The reaction mixture is stirred and heated at a temperature of 100° C. for 5 hours. The resulting terminally unsaturated polymer has an acid number of 0.8.

A portion of the above prepared polymer, comprising 440 parts is stirred together with a mixture of unsaturated monomers comprising 30 parts of 1,6-hexanediol dimethacrylate and 30 parts of lauryl methacrylate and 20 parts of 2,2-diethoxyacetophenone photoinitiator until it is completely homogeneous. A sample of the resulting photopolymer composition is stored in the dark for 50 days at a temperature of 60° C. After storage the composition is examined and found not to have gelled.

A sample of the above prepared photopolymer composition is poured into a rubber frame and a glass plate placed over the frame in contact with the composition. The composition is then exposed through the glass plate to ultraviolet light exactly as described in Example 1. A 0.017 inch layer of cross-linked (i.e. hardened) composition is formed next to the glass plate.

Specimens of the cross-linked photopolymer composition 50 mils thick are prepared and tested to determine physical properties exactly as described in Example 2. The cross-linked composition is found to have a tensile strength of 360 psi, an elongation of 70%, a tensile modulus of 736 psi, a Bayshore resilience of 37% and a Shore A hardness of 59. Specimens soaked in ethyl alcohol for 24 hours at room temperature gain 6% in weight. Specimens soaked in isopropanol under the same conditions gain 8% in weight.

EXAMPLE 5

This example illustrates the use of a liquid polymer prepared from amine terminated butadiene-acrylonitrile copolymer and gylcidyl methacrylate, in a photopolymer composition in accordance with this invention.

5

Into a flask equipped as described in Example 1 is charged 934.8 parts of an amine terminated butadiene-acrylonitrile copolymer (sold by B. F. Goodrich Co. under the trademark "Hycar ATBN"), 374 parts of glycidyl methacrylate and a mixture of thermal stabilizers comprising 0.07 part of nitrobenzene, 0.14 part of phenothiazine and 1.87 parts of di-tert-butyl-para-cresol. The reaction mixture is stirred and heated at a temperature of 60° C. for 4 hours.

A portion of the resulting terminally unsaturated polymer, comprising 246 parts is stirred together with a mixture of unsaturated monomers comprising 18 parts of 1,6-hexanediol dimethacrylate and 18 parts of lauryl methacrylate, 12 parts of 2,2-diethoxyacetophenone photoinitiator and 1.2 parts of di-tert-butyl-para-cresol stabilizer, for one hour at room temperature.

A 40 mil layer of the resulting photopolymer composition is cross-linked by exposure to a 3 kilowatt medium pressure mercury arc lamp for 3.5 minutes. Samples of the cross-linked composition are tested for physical properties and found to have a tensile strength of 2100 psi, an elongation of 32%, a tensile modulus of 23,200 psi, and a Shore A hardness of 88.

EXAMPLE 6

This example illustrates the use of the photopolymer composition described in Example 1 in the preparation of a printing plate.

6

ethyl cellosolve and 4% water. On completion of the press run the plate is visually examined and shows no sign of wear, swelling or tack. The printed impressions are of high quality.

EXAMPLE 7

This example illustrates the use of the terminally unsaturated polymer described in Example 1 in various photopolymer compositions.

In each case the terminally unsaturated polymer containing the mixture of thermal stabilizers as described in Example 1 is stirred with one or more unsaturated monomers and a photoinitiator to form a photopolymer composition. Samples for the testing of physical properties are spread to a thickness of 50 mils on a glass plate and covered with an 0.004 inch polyester film. Each sample is then exposed to ultraviolet light through the polyester film as described in Example 1 for one minute and then through the glass plate to a 3 kilowatt medium pressure mercury arc lamp for 4 minutes. Additional samples are prepared the same way except they are only exposed to the ultraviolet light through the polyester film for periods of time ranging from 30 to 180 seconds. The components of the photopolymer compositions, the thickness of the cross-linked layers formed on exposure for 30 to 180 seconds and the physical properties of the samples completely cross-linked are recited below in Table II.

TABLE II

Components of Photopolymer Composition	Parts per Hundred									
Terminally unsaturated polymer	88	88	88	88	88	88	88	88	88	77
Lauryl Methacrylate	6	4.2	7.8	6	6	6	6	6	12	—
1,6-Hexanediol dimethacrylate	6	7.8	4.2	6	6	—	—	—	—	23
Tetraethylene glycol dimethacrylate	—	—	—	—	—	6	—	—	—	—
Polypropylene glycol dimethacrylate	—	—	—	—	—	—	6	—	—	—
1,3-Butylene glycol dimethacrylate	—	—	—	—	—	—	—	6	—	—
2,2-Diethoxyacetophenone (photoinitiator)	4	4	4	6	—	4	4	4	4	—
Benzoin isobutyl ether (photoinitiator)	—	—	—	—	1.0	—	—	—	—	1.8
Thickness in mm of cross-linked layer after exposure for the following period of time:	Thickness in mm									
30 sec.	—	—	—	—	0.10	0.12	—	—	—	0.35
60 sec.	0.21	0.25	0.23	0.26	0.29	0.36	0.32	0.24	0.19	0.68
90 sec.	0.39	0.40	0.41	0.41	0.52	0.48	0.48	0.37	0.31	0.83
120 sec.	0.50	0.51	0.52	0.55	0.63	0.58	0.60	0.50	0.39	1.12
180 sec.	0.69	0.70	0.71	0.75	0.89	0.74	0.76	0.68	0.56	1.25
	Physical Properties									
Tensile Strength - psi[a]	220	230	200	230	220	180	170	270	150	—
Elongation - %	70	60	80	70	80	80	80	80	100	—
Tensile Modulus - psi	400	470	331	370	373	206	290	430	360	—
Shore A Hardness	47	52	42	42	46	42	40	48	44	83
Resilience - %	46	47	44	44	44	44	44	44	50	—
% Weight gain in ETOH[c]	2	2	2	2	2	4	4	2	2	3

[a]Tensile properties are measured with an Instron tester using 2 inches/min. crosshead speed.
[b]Resilience measured on a stack of 5 samples, each 50 mils thick, % return after steel ball dropped from 30 cm.
[c]Samples soaked in ethyl alcohol for 24 hours at a temperature of 25° C.

A portion of the photopolymer composition described in Example 1 is spread in a 0.067 inch thick layer on a 4 mil polyester backing sheet (support) and exposed through an image bearing negative transparency to a 3 kilowatt medium pressure mercury arc lamp for 6 minutes. The uncrosslinked photopolymer composition is washed away using an aqueous solution of 1.0% α-olefin sulfonate (Bioterg ®) at 50° C. The resulting printing plate is dried, and post-cured by exposing under a nitrogen atmosphere to a bank of 10 30-watt ultraviolet fluorescent lights for 12 minutes. The resulting printing plate is completely tack-free.

The thus prepared printing plate is mounted on a flexographic printing press and the press run at a speed of 250-300 fpm. until approximately 10,000 impressions are made. The ink used during the press run is a red flexographic ink containing as solvents 3% methyl alcohol, 73% ethyl alcohol, 10% isopropyl alcohol, 10%

EXAMPLE 8

This example illustrates the use of a vinyl terminated butadiene-acrylonitrile copolymer in a photopolymer composition in accordance with this invention.

A portion, comprising 77 parts, of a vinyl terminated butadiene-acrylonitrile copolymer (containing 17% acrylonitrile and having a number average molecular weight of approximately 3400) is stirred together with 23 parts of tetraethylene glycol dimethacrylate (unsaturated monomer), 1.8 parts of benzoin isobutyl ether (photoinitiator) and 0.1 part of di-tert-butyl-para-cresol (stabilizer) until the composition is completely homogeneous (about 1 hour).

The above prepared photopolymer composition is poured into a rubber frame, covered with a glass plate

7

and exposed to a bank of ultraviolet lights as described in Example 1. A layer 0.043 inch thick of cross-linked composition is formed. A sample of the cross-linked composition swelled 7% after soaking for 24 hours at room temperature in ethyl alcohol.

EXAMPLE 9

This example illustrates the use of a mixture of ethylenically unsaturated monomers containing N-vinyl-2-pyrrolidone in accordance with this invention.

A portion, comprising 520 parts of the terminally unsaturated polymer, prepared by reacting carboxyl terminated polybutadiene with glycidyl methacrylate as described in Example 1, is blended with a mixture of ethylenically unsaturated monomers comprising 144 parts of lauryl methacrylate, 60 parts of 1,3-butylene glycol dimethacrylate and 76 parts of N-vinyl-2-pyrrolidone and 4.8 parts of 2,2-dimethoxy-2-phenylacetophenone photoinitiator at room temperature until the mixture is completely homogeneous. The resulting photopolymer composition has a Brookfield viscosity measured at 25° C. of 4100 cps.

A sample of the photopolymer composition is spread to a thickness of 0.04 inch on a glass plate using a doctor blade, covered with a polyester film, exposed from both sides and tested to determine its physical properties, all as described in Example 2. The hardened resin has a tensile strength of 780 psi, an elongation of 83%, a tensile modulus of 813 psi, and a Shore A hardness of 64.
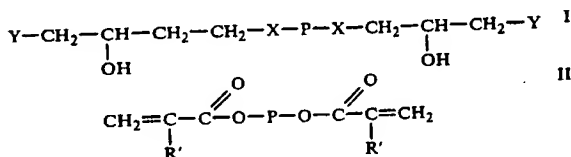
EXAMPLE 10

This example illustrates the use of an inert particulate filler in a photopolymer composition in accordance with this invention.
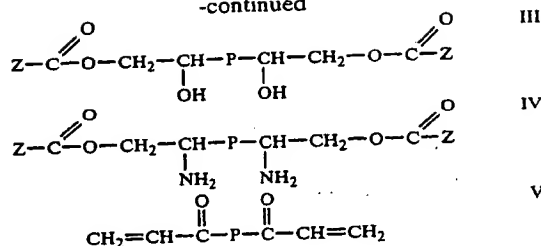
A portion, comprising 180 parts of the terminally unsaturated polymer described in Example 1, is blended with a mixture of ethylenically unsaturated monomers comprising 69 parts of lauryl methacrylate, 15 parts of 1,3-butylene glycol dimethacrylate and 36 parts of N-vinyl-2-pyrrolidone, 1.8 parts of 2,2-dimethoxy-2-phenylacetophenone photoinitiator and 13.1 parts of fumed silica particulate filler at room temperature until the mixture is completely homogeneous. The resulting photopolymer composition has a Brookfield viscosity measured at 25° C. of 6130 cps.

A 0.04 inch thick sample of the photopolymer composition is cured and tested to determine its physical properties, all as described in Example 2. The cured resin has a tensile strength of 630 psi, an elongation of 90%, a tensile modulus of 595 psi, and a Shore A hardness of 60.
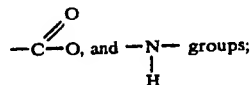
As stated above, the terminally unsaturated polymers used in the photopolymer compositions of this invention are liquid polymers containing at least two terminal olefin groups attached to the polymer through a combination of at least two ether, thioether, ester, keto or amide groups. These terminal olefinically unsaturated polymers will have one of the following structures
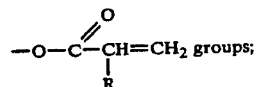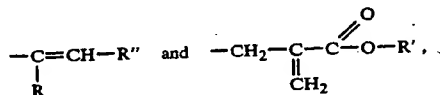
$$Y-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-X-P-X-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-Y \quad \text{I}$$

$$CH_2=\underset{\underset{R'}{|}}{C}-\overset{O}{\overset{\|}{C}}-O-P-O-\overset{O}{\overset{\|}{C}}-\underset{\underset{R'}{|}}{C}=CH_2 \quad \text{II}$$

8

-continued

$$Z-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{OH}{|}}{CH}-P-\underset{\underset{OH}{|}}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-Z \quad \text{III}$$

$$Z-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{NH_2}{|}}{CH}-P-\underset{\underset{NH_2}{|}}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-Z \quad \text{IV}$$

$$CH_2=CH-\overset{O}{\overset{\|}{C}}-P-\overset{O}{\overset{\|}{C}}-CH=CH_2 \quad \text{V}$$

where X is selected from —O—, —S—,

$$-\overset{O}{\overset{\|}{C}}-O, \text{ and } -\underset{\underset{H}{|}}{N}- \text{ groups;}$$

Y is selected from —O—CH_2—CH=CH_2 and

$$-O-\overset{O}{\overset{\|}{\underset{\underset{R}{|}}{C}}}-CH=CH_2 \text{ groups;}$$

R' is selected from —H and —CH_3 groups; Z is selected from

$$-\underset{\underset{R}{|}}{C}=CH-R'' \quad \text{and} \quad -CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{O}{\overset{\|}{C}}-O-R', $$

where R'' is selected from —H, —CH_3 and

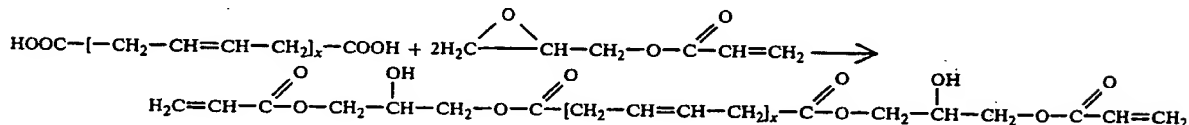$$-\overset{O}{\overset{\|}{C}}-O-R';$$

and P is a polymer residue selected from liquid homopolymers of butadiene, isoprene, chloroprene, styrene, isobutylene, ethylene and copolymers of butadiene with acrylonitrile, butadiene with styrene, butadiene with isoprene, ethylene with neohexene, isobutylene with styrene, and isobutylene with acrylonitrile and the corresponding saturated polymer residues. Preferably the above liquid polymers will have a molecular weight in the range of 1000 to 20,000, most preferably in the range of 3000 to 6000. It will be understood by those skilled in the art that if the polymer residue above was prepared by free radical polymerization, it may retain connecting groups originating from the free radical initiator employed in its preparation.

A typical liquid polymer employed in the photopolymer composition of this invention is one prepared by reacting a butadiene, isoprene, chloroprene, styrene, isobutylene, or ethylene polymer or a butadiene-acrylonitrile, butadiene-isoprene, butadiene-styrene, or ethylene-neohexene copolymer containing carboxyl, amine, hydroxyl, thiol, oxirane, or aziridine terminal groups, or corresponding products from which the olefinic unsaturation has been removed as by hydrogenation, with a glycidyl allyl ether, acrylate or alkyl substituted acrylate. Functionally terminated polymers and copolymers of the type useful for preparing these terminally unsaturated polymers are prepared by a free radical polymerization using special catalysts or by

anionic polymerization followed by capping the living polymer by carbon dioxide, ethylene oxide, etc. as described in an article by French in Rubber Chemistry and Technology, Vol. 42, pages 71-107 (1969). The step of adding the terminal unsaturated group to the functionally terminated polymer (i.e. the second step in
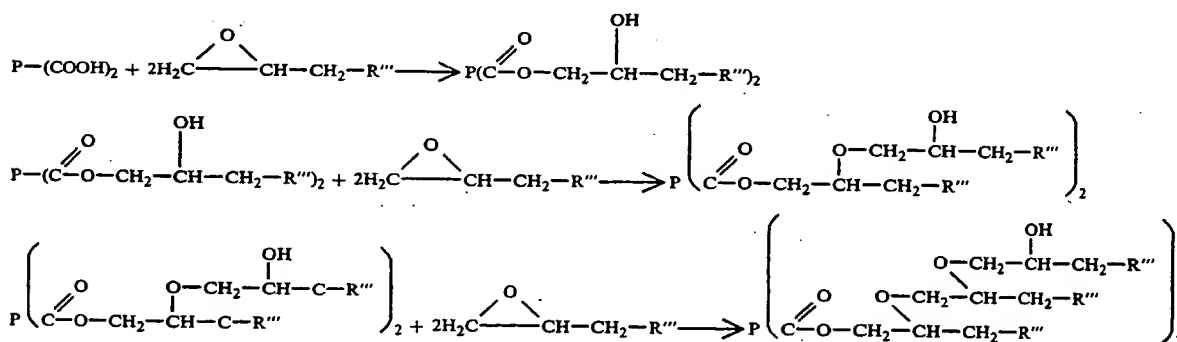
$$(C\diagdown O \diagup C - C - R''')$$

is represented below.

$$HOOC-[-CH_2-CH=CH-CH_2]_x-COOH + 2H_2C\diagdown O \diagup CH-CH_2-O-C\diagup O\diagdown CH=CH_2 \longrightarrow$$

$$H_2C=CH-C\diagup O\diagdown O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-O-C\diagup O\diagdown[CH_2-CH=CH-CH_2]_x-C\diagup O\diagdown O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-O-C\diagup O\diagdown CH=CH_2$$

preparing the terminally unsaturated polymer) is not a polymerization.

More particularly, the polymers of structure I can be prepared by reaction of functionally terminated or telechelic polymers of the type described by French in the Rubber Chemistry and Technology article referred to above, in which the terminal functional groups are carboxyl, hydroxyl, thiol or amine groups, with compounds such as allyl glycidyl ether, glycidyl acrylate,

As indicated two moles of epoxy compound react with each mole of olefin addition polymer. Generally, however, a slight excess of epoxide is used.

It is also possible to use a large excess of epoxy compound. In this case, chain extension occurs. The excess epoxide reacts with the hydroxyl groups formed by the initial reaction between the functionally terminated olefin addition polymer and the epoxy compound. For example:

$$P-(COOH)_2 + 2H_2C\diagdown O \diagup CH-CH_2-R''' \longrightarrow P(C\diagup O\diagdown O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-R''')_2$$

$$P-(C\diagup O\diagdown O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-R''')_2 + 2H_2C\diagdown O \diagup CH-CH_2-R''' \longrightarrow P\left(C\diagup O\diagdown O-CH_2-\underset{\underset{|}{O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-R'''}}{CH}-CH_2-R'''\right)_2$$

$$P\left(C\diagup O\diagdown O-CH_2-\underset{\underset{|}{O-CH_2-\underset{OH}{\underset{|}{CH}}-C-R'''}}{CH}-C-R'''\right)_2 + 2H_2C\diagdown O \diagup CH-CH_2-R''' \longrightarrow P\left(C\diagup O\diagdown O-CH_2-\underset{\underset{|}{O-CH_2-CH-CH_2-R'''}}{\underset{\underset{|}{O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-R'''}}{CH}}-CH_2-R'''\right)_2$$

glycidyl methacrylate, glycidyl crotonate, ethyl itaconate monoglycidyl ester or methyl fumarate monoglycidyl ester.

Polymers of structure II can be prepared by reaction of telechelic polymers containing hydroxyl functional groups with acrylic or methacrylic acid or the corresponding anhydride.

Polymers of structures III and IV can be prepared by reaction of telechelic polymers containing oxirane and aziridine functional groups, respectively, with unsaturated polymerizable acids such as acrylic, crotonic, methacrylic, or the monoalkyl esters of itaconic, or fumaric acid.

Polymers of the structure V are vinyl ketone terminated telechelic polymers.
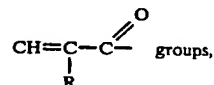
In general the terminal olefinically unsaturated polymers employed in the photopolymer composition of this invention are viscous liquids, having Brookfield viscosities, measured at 25° C., of between 1,000 and 1,000,000 centipoises, most preferably between 20,000 and 100,000 centipoises.

As an illustration of the type of reaction involved to introduce the terminal unsaturation into the low molecular weight polymers and copolymers to prepare the polymers useful for this invention, the reaction between a carboxyl terminated polybutadiene and glycidyl acrylate

These reactions can be run between 25° and 200° C. with a temperature range of 100°-125° being preferred. An acid or basic catalyst can be used to reduce the required reaction temperature and time. Some useful catalysts are sodium hydroxide, sodium ethoxide, triethylamine, triethylbenzyl ammonium chloride, hydrogen chloride, and boron trifluoride etherate. Generally, 0.001 to 5.0% by weight catalyst is used.

To make the polymer with only single terminal double bonds, close to a stoichiometric amount of epoxide and a basic catalyst should be used. To make a chain extended polymer, a large excess of epoxide and an acidic catalyst is preferred.

The ethylenically unsaturated monomer components of the compositions of this invention are selected from acrylonitrile, methacrylonitrile, styrene, methyl substituted styrenes, N-vinyl pyrrolidone, and compounds containing one or more
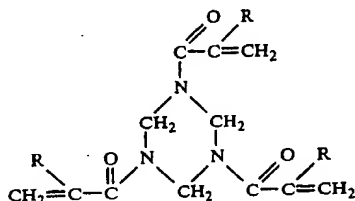
$$\underset{R}{\underset{|}{CH=C-C}}\diagup O\qquad groups,$$

wherein R is hydrogen or a C_1-C_3 alkyl group.

Useful monofunctional ethylenically unsaturated monomers include acrylonitrile, methacrylonitrile, styrene, 2-methylstyrene, α, p-dimethylstyrene, N-vinyl pyrrolidone, acrylic acid, methacrylic acid, esters of acrylic acid and methacrylic acid containing up to 22
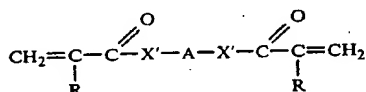
carbon atoms, acrylamide, mono- and di-N-alkyl substituted acrylamides and methacrylamides containing up to 10 carbons in the alkyl group, and diacetone acrylamide.

A useful trifunctional monomer is 1,3,5-triacryloyl-hexahydro-1,3,5-triazine. This compound and related compounds such as the corresponding methacryloyl derivative have the structural formula
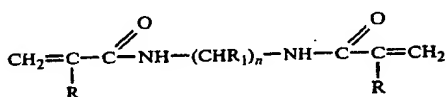
$$
\begin{array}{c}
\text{I}
\end{array}
$$

wherein R is hydrogen or a C_1-C_3 alkyl group.

Other suitable difunctional monomers may be defined by the structural formula

$$
CH_2{=}C{-}C{-}X'{-}A{-}X'{-}C{-}C{=}CH_2 \qquad \text{II}
$$

wherein R again is hydrogen or a C_1-C_3 alkyl group; both X's are either —NH— or —O— and A is alkylene, substituted alkylene or alkylene oxy alkylene. A preferred monomer having this formula is N,N'-oxydimethylene-bis(acrylamide).

When X' in formula II above is —NH—, but A is alkylene or substituted alkylene, this is descriptive of another preferred monomer, N,N'-methylene-bis(acrylamide). This compound is one member of a valuable group of monomers represented by compounds having the formula
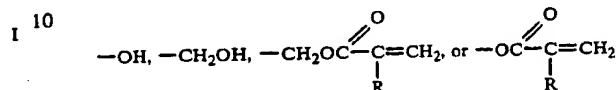
$$
CH_2{=}C{-}C{-}NH{-}(CHR_1)_n{-}NH{-}C{-}C{=}CH_2 \qquad \text{III}
$$

wherein R is hydrogen or a C_1-C_3 alkyl group, R_1 is hydrogen, a C_1-C_3 alkyl group or phenyl, n is 1 to 6 and the total number of carbon atoms in —$(CHR_1)_n$— is no more than 10.

Representative of compounds of formula III above are N,N'-methylene-bis(acrylamide), N,N'-methylene-bis(methacrylamide), N,N'-methylene-bis(2-ethyla-crylamide), N,N'-methylene-bis(2-propylacrylamide), N,N'-ethylene-bis(acrylamide), N,N'-ethylene-bis-(methacrylamide), N,N'-(1,6-hexamethylene)-bis(acrylamide), N,N'-(1,6-hexamethylene)-bis(methacrylamide), N,N'-ethylidene-bis-(acrylamide), N,N'-ethylidene-bis(methacrylamide), N,N'-benzylidene-bis(acrylamide), N,N-butylidene-bis(methacrylamide) and N,N'-propylidene-bis(acrylamide). These compounds may be prepared by conventional reactions well known in the art, as for example, in U.S. Pat. No. 2,475,846.
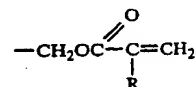
Also useful monomers are those wherein X' in formula II above is —O—. When A is alkylene or substituted alkylene, the compounds are di-, tri- and tetra-acrylates of certain polyhydric alcohols. These acrylates may be illustrated by the general formula

$$
CH_2{=}C{-}C{-}O{-}(CH_2)_{\overline{a}}{-}(CR_2R_3)_{\overline{n}}{-}(CH_2)_{\overline{a}}{-}O{-}C{-}C{=}CH_2 \qquad \text{IV}
$$

wherein R is hydrogen or a C_1-C_3 alkyl group, a is 0 or 1, R_2 is hydrogen, a C_1-C_3 alkyl group,

$$
-OH, -CH_2OH, -CH_2OC{-}C{=}CH_2, \text{ or } -OC{-}C{=}CH_2
$$

R_3 is hydrogen, a C_1-C_3 alkyl group, —CH_2OH or

$$
-CH_2OC{-}C{=}CH_2,
$$

n is 1 to 6 and the total number of carbon atoms in —$(CR_2R_3)_n$— is no more than 11. Representative of these compounds are ethylene glycol diacrylate, ethylene glycol dimethacrylate, ethylene glycol di(2-ethyla-crylate), ethylene glycol di(2-propylacrylate), 1,3-pro-pylene glycol diacrylate, 1,4-butylene glycol diacrylate, 1,5-pentanediol dimethacrylate, glycerol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetramethacrylate and pentaerythritol tetraacrylate.

Closely related to the preceding acrylates are those which are derived from di-, tri- and tetra-ethylene glycol and di- and tri-propylene glycol. These compounds are those of formula II wherein X' is —O— and A is alkylene oxy alkylene, and they may be more specifically illustrated by the formula

$$
CH_2{=}C{-}C{-}O{-}(CHR'CH_2O)_n{-}C{-}C{=}CH_2 \qquad \text{V}
$$

wherein R is hydrogen or a C_1-C_3 alkyl group, R' is hydrogen or methyl, n is 2 to 4 when R' is hydrogen and is 2 to 3 when R' is methyl. Representative of these compounds are diethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, dipropylene glycol diacrylate, dipropylene glycol dimethacrylate, tripropylene glycol diacrylate and tripropylene glycol dimethacrylate.

While a single unsaturated monomer may be employed alone in the photopolymer composition, mixtures of two or more monomers are generally employed together to obtain best results. In any event the amount of monomer or monomers used to effect crosslinking of the polymer component of the compositions of this invention will be from about 1 to about 50%, most preferably from about 5 to about 25%.

The photoinitiators useful in the photopolymer compositions of this invention are generally well known and some are characterized by being photoreducible. They are compounds which absorb actinic light very strongly and thus become activated to the point where they will abstract hydrogen atoms from compounds which are

13

hydrogen donors. By so doing, the photoinitiator is itself reduced and the hydrogen donor is converted into a free radical. Representative compounds are benzophenone, 2-chlorobenzophenone, 4-methoxybenzophenone, 4-methylbenzophenone, 4,4'-dimethylbenzophenone, 4-bromobenzophenone, 2,2',4,4'-tetrachlorobenzophenone, 2-chloro-4'-methylbenzophenone, 4-chloro-4'-methylbenzophenone, 3-methylbenzophenone, 4-tert-butylbenzophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin acetate, benzil, benzilic acid, methylene blue, acetophenone, 2,2-diethoxyacetophenone, 9,10-phenanthrenequinone, 2-methyl anthraquinone, 2-ethyl anthraquinone, 2-tert-butyl-anthraquinone, and 1,4-naphthoquinone. Particularly suitable are 2,2-diethoxyacetophenone, benzoin isopropyl ether, benzoin isobutyl ether, and 2-ethyl anthraquinone. Also applicable are combinations of carboxyl sensitizer compounds and certain organic amine activators as disclosed in U.S. Pat. No. 3,759,807. In general, the photoinitiator should be thermally stable at temperatures up to about 100° C. Stability at such temperatures prevents premature crosslinking when the compositions of this invention are prepared or during storage. Such stability also minimizes, during exposure, any crosslinking in the unexposed areas caused by the heat generated in the crosslinking reaction and by the heat transmitted through the opaque sections of the transparency. The amount of photoinitiator will be from about 0.1 to about 10%, most preferably from about 1.0 to about 10% by weight based on the weight of the polymer in the photopolymer composition.

For the purpose of inhibiting premature crosslinking during thermal processing and storage of the photopolymer compositions of this invention, the incorporation of a thermal polymerization inhibitor and inhibitors is desirable. Such stabilizers also are well-known in the art, and they are exemplified by di-t-butyl-p-cresol, hydroquinone monomethylether, pyrogallol, quinone, hydroquinone, methylene blue, t-butyl catechol, hydroquinone monobenzyl ether, methyl hydroquinone, amyl quinone, amyloxy hydroquinone, n-butyl phenol, phenol, hydroquinone monopropyl ether, phenothiazine and nitrobenzene, used separately or in combination. When used in an amount within the range of from about 0.01 to about 2% by weight of the polymer, these stabilizers are quite effective in preventing crosslinking of the photopolymer composition during processing and storage. During exposure such amounts of stabilizer also delay and thus prevent crosslinking due to scattered light in the nonexposed areas of the composition, but do not greatly interfere with or delay the crosslinking of the composition in strongly exposed areas, thus aiding in formation of a plate of optimum depth and surface configuration.

The photopolymer compositions also may contain up to about 55% by weight of an inert particulate filler which is essentially transparent to actinic light. Representative of such fillers are the organophilic silicas, the bentonites, silica and powdered glass, all having a particle size less than 0.4 mil in their maximum dimension. Particles of 0.1 micron or less in size are preferred. Such fillers can impart desirable properties to the compositions and reliefs of this invention. Furthermore, the light scattering effected by the particulate fillers broadens the image toward the base of the plate so that the half-tone dots take on the appearance of truncated cones in cross-section. Such dots are stronger and have
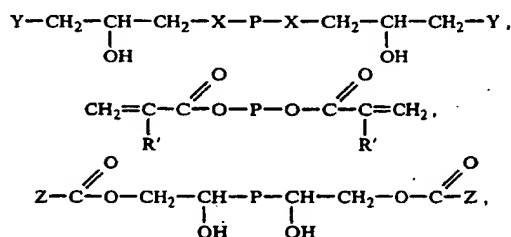
14

less tendency to break off than dots which are more cylindrical in cross-section.

When the photopolymer compositions of this invention are exposed to actinic light at a wave length of from about 3000 to about 4000 Å through a photographic negative or positive, the polymer beneath the exposed areas becomes insolubilized, whereas the polymer beneath the unexposed areas remains water dispersible. Subsequent washing of the plate removes the dispersible polymer, leaving a replica of the negative or positive in relief. Washing will normally be carried out with dilute aqueous solution of an anionic or nonionic detergent. Anionic detergents such as α-olefin sulfonates, alkylaryl sulfonates, lauryl sulfate, alkyl esters of sulfosuccinic acid, or sulfated ethylene oxide condensates of alkyl phenols or fatty alcohols, and nonionic detergents such as alkyl phenol, fatty alcohol or fatty acid ethylene oxide condensates may be used. α-olefin sulfonates are particularly useful. Detergent concentrations of about 0.2 to 2% will normally be employed, generally at temperatures of 25°–60° C. Development may frequently be accelerated by brushig or scrubbing. In large scale work, application of the water solvent will advantageously be carried out by means of jets or sprays. In some instances, it may be helpful to use minor quantities of organic solvents such as the short chain aliphatic alcohols and ketones. Suitable solvents of these types include methanol, ethanol and acetone, and they generally will be used in amounts no greater than 25–35%, preferably less than 1–5% of the water or aqueous detergent developer. Following development of the plate, residual surface water, and any organic solvent which also might be present, may be removed by passing a current of warm air over the relief. In some instances it may be desirable to post-expose or post-cure the plates by exposing to actinic light at the wave lengths recited above, after the uncrosslinked photopolymer composition has been washed away.

The printing reliefs made in accordance with this invention are most applicable to those wherein a distinct difference in height between printing and non-printing areas is required. These classes include those wherein the ink is carried by the raised portion of the relief, such as in dry off-set printing and ordinary letter-press printing. Because of the flexibility, abrasion resistance, resilience, and alcohol resistance of the relief plates prepared using these compositions, they are particularly useful for flexographic printing in which alcohol based inks are employed.
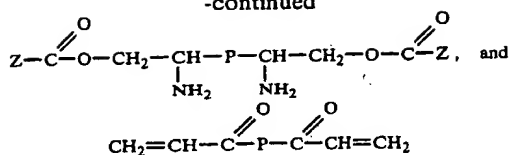
What I claim and desire to protect by Letters Patent is:

1. A photopolymer composition comprising (1) a liquid terminal olefinically unsaturated linear polymer having a molecular weight in the range of from 1,000 to 20,000, selected from polymers having the structure
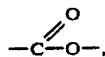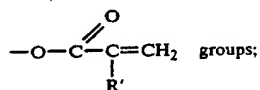
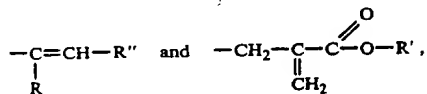$$Y-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-X-P-X-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-Y,$$

$$CH_2=\underset{\underset{R'}{|}}{C}-\overset{O}{\overset{\|}{C}}-O-P-O-\overset{O}{\overset{\|}{C}}-\underset{\underset{R'}{|}}{C}=CH_2,$$

$$Z-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{OH}{|}}{CH}-P-\underset{\underset{OH}{|}}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-Z,$$

15

-continued

$$Z-C(=O)-O-CH_2-CH(NH_2)-P-CH(NH_2)-CH_2-O-C(=O)-Z, \text{ and}$$

$$CH_2=CH-C(=O)-P-C(=O)-CH=CH_2$$

where X is selected from —O—, —S—,

$$-C(=O)-O-,$$

and —NH— groups; Y is selected from —O—CH$_2$—CH=CH$_2$ and

$$-O-C(=O)-C(R')=CH_2 \quad \text{groups;}$$

R' is selected from —H and —CH$_3$ groups; Z is selected from

$$-C(R)=CH-R'' \quad \text{and} \quad -CH_2-C(=CH_2)-C(=O)-O-R',$$
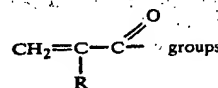
where R'' is selected from —H, —CH$_3$ and

$$-C(=O)-O-R';$$

and P is a polymer residue selected from homopolymers of butadiene, isoprene, chloroprene, styrene, isobutylene, ethylene, and copolymers of butadiene with acrylonitrile, butadiene with styrene, butadiene with isoprene, ethylene with neohexene, isobutylene with styrene, isobutylene with acrylonitrile, and the corresponding saturated residues; (2) from about 1 to about 50% by weight based on the weight of the polymer of at least one ethylenically unsaturated monomer selected from acrylonitrile, methacrylonitrile, styrene, methyl substi-

16

tuted styrene, N-vinyl pyrrolidone, and monomers containing one or more

$$CH_2=C(R)-C(=O)- \quad \text{groups}$$

wherein R is hydrogen or a C$_1$–C$_3$ alkyl group; (3) from about 0.1 to about 10% by weight based on the weight of the polymer of a photoinitiator; and (4) from about 0.01 to about 2% by weight based on the weight of the polymer of a stabilizer.

2. The composition of claim 1 wherein the liquid terminal olefinically unsaturated polymer is the reaction product of carboxyl terminated polybutadiene and glycidyl methacrylate.

3. The composition of claim 1 wherein the liquid terminal olefinically unsaturated polymer is the reaction product of carboxyl terminated butadiene-acrylonitrile copolymer and glycidyl methacrylate.

4. The composition of claim 1 wherein the liquid terminal olefinically unsaturated polymer is the reaction product of amine terminated butadiene-acrylonitrile copolymer and glycidyl methacrylate.

5. The composition of claim 1 wherein the liquid terminal olefinically unsaturated polymer is vinyl terminated butadieneacrylonitrile copolymer.

6. The composition of claim 1 wherein the ethylenically unsaturated monomer is a mixture of 1,6-hexanediol dimethacrylate and lauryl methacrylate.

7. A photopolymer element comprising a support and a layer comprising the photopolymer composition of claim 1.

8. The photopolymer element of claim 7 wherein the layer comprising the photopolymer composition of claim 1 is a relief height-forming layer.

9. The photopolymer element of claim 7 wherein said support is a polyester sheet.

10. The photopolymer element of claim 7 wherein said photopolymer composition layer contains up to 55% by weight of an inert particulate filler essentially transparent in the layer.

* * * * *